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CERAMICS

CLAY TECHNOLOGY

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BY

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FIRST EDITION
FIFTH IMPRESSION

BILLS
CLARK

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK AND LONDON
1927

WITHDRAWN

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McGraw-Hill Book Company, Inc.

PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

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92716

PREFACE

For many years a need has existed for a text on clay technology which could be used in university work as an introduction to the field of ceramic engineering. The following is a summary of data collected from ceramic literature, commercial factory practice and experiences in the class rooms of the Ohio State University and the University of Washington. At the latter institution, these notes now cover the introductory ceramic lecture and recitation work for three school quarters of three credit hours each, when used with the report of the Committee on Standards of the American Ceramic Society for the methods of clay testing, with "Non-metallic Minerals" by Raymond B. Ladoo for the associated non-metallics, and with the book on "Clays" by Heinrich Ries for the occurrence of clays.

Very little mention has been made of ceramic manufacturing processes or clayworking equipment for this has been the favorite subject of previous ceramic authors.

ACKNOWLEDGMENTS

Complete acknowledgment cannot be made without reference to all the many contributors to our ceramic literature from the time of Hermann A. Seger to the present. The publication of the American Ceramic Society, the English Ceramic Society, and the various American, German, French, and Japanese technical trade magazines are veritable treasure chests of heterogeneous mixtures of articles on all phases of ceramics. An effort has been made to include those portions which have played or will play important roles in the advancement of ceramic engineering. Naturally, personal experiences and training have colored the whole.

Particular emphasis should be given in these acknowledgments to certain individuals whose work has been of fundamental character; to Prof. Edward Orton, Jr., formerly of the Ohio State University, who perfected a classification of clays and an understanding of the effect of heat on clays, and who put ceramic engineering on a firm foundation in this country through his

University work and as the first secretary of the American Ceramic Society; to Albert V. Bleininger, who as director of ceramic research at the United States Bureau of Standards gave a fundamental concept of the structure of plastic clay, the effect of electrolytes, and the action of pressure combined with heat on clays; to Dr. Heinrich Ries for his studies on the geology and distribution of clays; to Dr. J. W. Mellor, the English ceramist and chemist, who has done wonderful work in the chemistry of clay and pottery materials; to Dr. E. C. Bingham for his work on the mechanism of plasticity; to Dr. W. D. Bancroft and other colloid chemists for a better, though still imperfect, understanding of the colloidal nature of clays; to H. G. Schurecht, who gave the most accurate measurement of the size of clay particles; and to the present members of the United States Bureau of Standards and engineers of the Carrier Engineering Corporation, who are revolutionizing antiquated drying systems and methods.

The former members of the short-lived United States Bureau of Mines ceramic section, R. T. Stull, G. A. Bole, F. G. Jackson, and others, have given fundamental data on combustion in kiln firing and the oxidation of the carbon, sulphur, and iron impurities in clays. The work of Herman A. Seger is still a standard reference for data on the relation between the fired colors of clay and their chemical composition and likewise for data on soluble salt impurities. Dr. E. W. Washburn and his former University of Illinois ceramic coworkers gave a better concept of porosity and more accurate methods of its measurement.

N. L. Bowen and other members of the Geophysical Laboratory, Carnegie Institute of Washington, have laid an excellent foundation in pyrochemical silicate reactions, melting, and crystallization phenomena. The importance of their data has not yet been realized, but as ceramists become more deeply interested in crystalline silicates and allied materials and work more with synthetic compounds than with mechanical, natural mixtures, they will find that the new paths have been well charted. A large amount of data on the viscosity-temperature relationships of silicates is still necessary, and Prof. Arthur S. Watts and his students of the Ohio State University have been collecting valuable data of direct importance to the amorphous or vitreous silicate field. The recent data of C. O. Fairchild and M. F. Peters of the United States Bureau of Standards have increased respect for this humble but yet most satisfactory method of

measuring the firing progress of a kiln, but the tests should be continued under various commercial conditions. A thorough classification of dryers and kilns has been made by Ellis Lovejoy.

Some members of the ceramic family collect fundamental data. Others make technological and commercial applications. There must be a guiding spirit, however, to provide the enthusiasm, the coordination, the collection, the assembling and distribution of labors, and for this purpose a most resourceful leader is found in Ross C. Purdy, general secretary of the American Ceramic Society.

HEWITT WILSON.

SEATTLE, WASH.,
August, 1927.

INTRODUCTION

Although clay-working is one of the oldest industries of man and has progressed through the centuries, yet its technical development has been slow when compared with many younger industries which may be called the children of modern engineering and chemical research. This is probably due to the inadequacy of the contemporary general research when applied to the ceramic problems of suspensions, plastic working conditions, and silicate fusions. The older industries which started before the days of modern chemistry and physics have had the handicap of mediæval methods, superstitions, trade secrets, and prejudices not known to the younger industries. Ceramics has been particularly unfortunate in this respect. The artistic side of pottery ceramics was highly developed centuries ago. The original potter's wheel, a flat stone pivoted on to another stone and turned by hand to shape round vases and bowls, is thought by some to have been man's first machine, from which have developed the rotating and circular movements of all the present machinery. Other phases of the early ceramic development are likewise lost in antiquity.

Practical experience and "cut-and-try" methods are still the principal factors in commercial research. It is only since the development and generalization of colloid chemistry that ceramists have had a tangible theory of the structure and properties of their heterogeneous plastic materials. They have had to wait until modern physical chemistry became interested in the great world of small particles, films, and drops. Since the firing of the first common brick, clayworkers have made use of the pyrochemical reactions of high-temperature silicate chemistry without understanding anything but the physical results produced. This is largely true at the present time. The natural silicates are so varied and complex that their disentanglement has only begun. General chemistry has likewise left this field almost untouched until this late day. The Geophysical Laboratory of Washington and the general metallurgical industry have contributed to the knowledge of the melted and fused silicates. The

difficulties of experimentation at high temperatures had been increased by the inaccurate methods of the past for measuring high temperatures and the maintenance and duplication of uniform conditions.

Mechanical Progress.—The field of glass ceramics has progressed wonderfully in the last 25 years because of the replacement of hand methods by mechanical apparatus. The pottery industry has just started on its mechanical renaissance. The brick and tile industries need new methods of handling ware after molding. Mechanical "hands" are being developed at the present time for removing stiff-mud brick from a conveyor belt and packing them on a dryer car. The labor and fuel costs of brick manufacture amount to approximately 70 per cent of the total. Mining, grinding, and the transportation of raw materials have been developed to efficient standards. Likewise, the continuous and railroad tunnel kilns, which give a saving of from 40 to 70 per cent in fuel compared to the periodic kilns, are now in common use. As soon as molded, glass articles are hard enough to be handled mechanically. Pottery, when shaped and dried in plaster molds, can be handled on mechanical conveyors, but ware which is dried without molds must still be picked up and laid down by the human hand. Architectural terra cotta is dependent on the hand method of molding.

Standard Tests of Materials and Products.—Although clays have been tested by numerous practical methods since early history, standard methods were not devised and approved by the American Ceramic Society until 1921–1922. The lack of universal standards and methods of testing clay products has been a great handicap in the development of structural clay wares. In the case of refractory clay wares, fundamental investigations were found necessary in the field of high-temperature measurement, effect of load, gas and slag action, thermal shock, abrasion, etc., before the first tests and standards could be devised. And it is now found that an enormous task has only been started. The United States Bureau of Standards, the American Ceramic Society, the Mellon Institute of Industrial Research, and the American Society for Testing Materials have all contributed to the production of standard tests. And it is through the development of standards for products that a great deal is learned of the fundamentals of raw materials and their manufacture.

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CERAMICS
CLAY TECHNOLOGY

CHAPTER I

GENERAL CERAMICS

A. DEFINITION AND ETYMOLOGY OF THE WORD "CERAMICS"

Although at one time[1] the name "Ceramic" was thought to refer only to the art of pottery, current usage has broadened the term to include all silicate industries. The etymology of the term[2] shows that it has been derived from the Greek word "keramos," now commonly meaning "a potter," "potter's clay," or "pottery," but that the Greek word is related to an older Sanskrit root, meaning "to burn" and, as used by the Greeks themselves, its primary meaning was simply "burnt stuff." The fundamental idea contained in the word was that of a product obtained through the action of fire upon earthy material.

As now accepted,[3] two characteristic elements are involved: first and primarily, a product in whose manufacture a high-temperature treatment is involved; and secondarily, a product customarily manufactured entirely or chiefly from raw materials of an earthy nature, as distinguished from those of an organic and metallic nature. This definition is so broad that it covers nearly one-third of the field of industrial activity as indicated in the following list of products which are now classified as *ceramic:*

[1] "Handbook of the American Ceramic Society," 1919.

[2] OLDFATHER, W. A.: "Etymology of the Word 'Ceramic,'" *J. Am. Ceram. Soc.*, **3**, 537 (1920).

[3] *Report* of the Committee on Definition of the Term "Ceramics," *J. Am. Ceram. Soc.*, **3**, 526 (1920).

B. CLASSIFICATION OF CERAMIC PRODUCTS

TABLE I

STRUCTURAL CERAMICS:

1. Common brick
2. Paving brick
3. Face brick
4. Sewer pipe
5. Drain tile
6. Hollow block
7. Terra cotta
8. Conduits
9. Roofing tile
10. Flue lining
11. Floor tile
12. Wall and fireplace tile

REFRACTORIES:

13. Fire-clay brick
14. Magnesia brick
15. Silica brick
16. Chromite brick
17. Bauxite and diaspor brick
18. Special refractories

POTTERY:

19. Tableware
20. Kitchen ware
21. Art pottery
22. Sanitary ware
23. Stoneware
24. Chemical porcelain and stoneware

GLASS:

25. Household
26. Window
27. Bottle
28. Lighting
29. Optical glass
30. Glazes, enamels, and artificial stones
31. Quartz glass

ENAMELED METALS:

32. Household and kitchen
33. Sanitary
34. Chemical
35. Advertising

ABRASIVES:

36. Silicon carbide
37. Aluminous abrasives

CEMENTS, LIMES, AND PLASTERS:

38. Portland cement
39. Building, agricultural, and chemical lime
40. Calcined gypsum products
41. Magnesia cement
42. Dental cement

INSULATION:

43. Electrical insulators
44. Thermal insulators

The ceramic products in the above list can be divided again into three different groups, according to the methods used in manufacture and the process of hardening after molding.

1. Those products which are molded in the aqueous plastic condition and which derive their strength from the partial fusion (vitrification) of silicates at high temperatures. This group is composed of structural, pottery, refractory, abrasive, and insulation products in which clay

is the principal ingredient or in which fused silicates provide the fired strength. The units are made in factories and with the exception of pottery are assembled on the job into a permanent structure with a cementitious binder.

2. Those products which are heated until they become fluid and are molded in the viscous liquid state. The final strength is obtained by cooling. Glass.

3. Those pulverized products in which the raw materials acquire by heating a latent cementitious property which becomes active on the addition of water. Only the cementitious portion is factory made, and the final product is shaped and hardened on the job. Cements, limes, and plasters.

C. DESCRIPTION OF CERAMIC PRODUCTS

TABLE II

Raw Material	Color Fired	Distinguishing Features	Uses
1. STRUCTURAL WARES			
1. COMMON BRICK			
Surface, glacial, or alluvial clays, sometimes shales	Dark, red and brown	Cheapness, usually possessing a soft, open structure	Backing material for walls
2. PAVING BRICK			
Shales, most common	Dark, red brown	Vitrified structure, strong and tough to resist abrasion, usually equipped with side lugs	Paving
3. FACE BRICK			
Variety of clays and shales	Cream to dark	Attractive color and finish	Facing for wall construction
4. SEWER PIPE			
Shales, primary; soft clays or low grade fire clays, secondary	Dark, red brown	Salt-glazed surface, circular cross-section, flanged end	Sewer drainage
5. DRAIN TILE			
Surface, glacial, or alluvial clays, sometimes shales	Dark	Cheapness, circular cross-section	Agricultural drainage
6. HOLLOW BLOCK, FIREPROOFING, ETC.			
The hollow substitute for common and face brick; see Nos. 1 and 3		Rectangular, hollow construction	Backing as in No 1 Facing as in No. 3
7. TERRA COTTA (ARCHITECTURAL)			
A mixture of buff burning, usually lower grade fire clays, with from 25 to 50 per cent calcined material		Hollow construction, variety of shapes, textures, and glazed colors	Primary, facing material; secondary, interior decoration
8. CONDUITS			
See No. 4; special rectangular shapes for carrying underground wiring			

9. ROOFING TILE			
See Nos. 3 and 6; usually dark color though sometimes buff		Shingle shape; may be glazed or colored	Roofing material
10. FLUE LINING			
Lower grades of refractory clays	Brown or buff	Hollow cross-section, refractory qualities	Chimney linings
11. FLOOR TILE			
Synthetic body of feldspar, clay, and flint	White or colored	Vitrified, dense, tough, and strong to resist abrasion; see No. 2	Flooring, mainly interior
12. WALL AND FIREPLACE TILE			
See No. 11	White or colored	Commonly a porous body glazed to any color	Wall facing, primarily for interior, though used for store fronts

2. Refractories

13. FIRE-CLAY BRICK			
Fire clay, usually grogged	Cream, buff, or brown	Refractoriness, special shapes and properties for specific uses	Metallurgical furnaces, ovens, boilers, fireplaces, etc.
14. MAGNESIA BRICK			
Magnesite, calcined with 4–10 per cent Fe_2O_3	Dark, red brown	Basic refractoriness	Side walls and bottoms of metallurgical furnaces
15. SILICA BRICK			
Quartzite with 2 per cent CaO, totalling 95 per cent SiO_2	Light cream or gray	Acid refractoriness; expansion at high temperatures	Roof and wall construction of metallurgical furnaces
16. CHROMITE BRICK			
Chromite ore	Black	Neutral refractoriness	Metallurgical furnaces
17. BAUXITE AND DIASPOR BRICK			
Diaspor bauxite, laterite, gibbsite, etc.	Buff and brown	Refractory qualities	Metallurgical furnaces

18. SPECIAL REFRACTORIES

Lime, zirconia, rare earths, certain carbides and nitrides, aluminum and silicon carbide, spinels, sillimanite, and other electric furnace products (see Abrasives).

3. Pottery

19. TABLEWARE			
Synthetic mixture of feldspar, clay, and flint with other fluxes	White or cream	Purity of color and translucent body for best grades; pleasing shapes and decorations	Tableware
20. KITCHEN WARE			
Plastic buff or gray-burning clays or shales, for (*a*), (*b*), (*c*), and (*d*). Red-burning clays common for (*c*) and (*d*)		Glazed and colored; cooking ware should be resistant to temperature changes	(*a*) Mixing bowls (*b*) Milk crocks (*c*) Baking dishes (*d*) Teapots

21. ART POTTERY

All variety of clays are used for art ware; the value depends on the artistic texture, color, or decoration of the surface or shape of the piece

22. SANITARY WARES

See No. 7; buff-burning grogged bodies, or white-ware body	Glazed with white, opaque enamels	Bathroom, toilet, or laundry wares

23. STONEWARE

See No. 20 Plastic buff or gray-burning clays or shales	Vitrified body, glazed gray buff or near white	Jars and crocks

24. CHEMICAL PORCELAIN AND STONEWARE

See Nos. 19 and 23, respectively White or gray buff	Glazed to be resistant to various chemicals	Chemical manufacture or storage

4. Glass

25, 26, 27, 28, 29. Household, Window, Bottle, Lighting, and Optical Glass

Synthetic mixtures of pure silica sand (around 75 per cent) with variable amounts of alkalies, calcium, magnesium, barium, or lead oxides, or other fluxes, but with a low alumina content. The mixture is heated to a state of complete fusion and shaped while in the plastic molten condition and then annealed. The compositions vary widely for the production of various shapes, or optical properties.

30. Glazes, Enamels, and Artificial Stones

Various silicate compositions, similar to the glasses above, but containing higher alumina contents. Used for covering clay and metal wares or shaped alone.

31. Quartz Glass

Pure silica sand, fused in the electric furnace, to produce a glass which is resistant to high temperatures and sudden thermal changes. It is used for laboratory articles, pyrometer tubes, etc.

5. Enameled Metals

32, 33, 34, 35. Household, Kitchen, Sanitary Chemical, and Advertising

Glazed metals. The enamel itself is a ceramic material applied at a high temperature to the metal, which gives the desired form and strength to the glass. A combination of the sanitary and coloring properties of a glass with the strength and rigidity of cast iron, steel, bronze, etc.

6. Abrasives

36. Silicon Carbide (Carborundum, Crystolon, Etc.)

Electric-furnace product formed by heating pure silica sand with carbon to produce crystalline SiC. Crushed, ground, mixed with plastic material, shaped, and fired for strength. Can be used as a refractory as well as an abrasive material.

37. Aluminous Abrasives (Alundum, Aloxite, Etc.)

Electric-furnace product formed by fusing high aluminous ores such as bauxite, to produce alumina of high purity. Crushed, ground, mixed with plastic material, shaped, and fired for strength. Used for refractory and abrasive purposes.

7. Cements, Limes, and Plasters

38. Portland Cement

"Portland cement is the product obtained by finely pulverizing clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum."[1] The ratio of the silica, alumina, and iron oxides to the line is approximately 1:2.

39. Building, Agricultural, and Chemical Lime, CaO

Product obtained by heating relatively pure limestone, $CaCO_3$, to form quicklime, CaO. When mixed with water, it slakes, forming calcium hydroxide, $Ca(OH)_2$, but does not show hydraulic properties. Hardens after partial drying and absorption of carbon dioxide from the atmosphere.

40. Calcined Gypsum Products (Molding and Bulding Plaster and Stucco)

Product obtained by heating the finely pulverized gypsum, $CaSO_4.2H_2O$, to above 107° C. to drive off three-fourths (calcined gypsum) or all of the combined water (soluble anhydrite). Retarders, accelerators, and fillers may be added to produce special properties of time of setting and hardness.

41. Magnesia Cement (Sorel Cement)

A mixture of lightly calcined magnesite with magnesium chloride, producing hydrated magnesia-oxychloride, $MgCl_2.3MgO$. ZnO and $ZnCl_2$, etc., behave in a similar manner.

42. Dental Cements

Mixtures of zinc oxide with phosphoric acid or mixtures of various silicates and orthophosphoric acid for use in dentistry.

8. Insulation Products

43. Electrical Insulators (Porcelain Spark Plugs, Etc.)

See No. 19. Porcelains of special composition designed to give high electrical resistance and mechanical strength.

44. Thermal Insulators (Diatomaceous Earth Brick)

a. Sawed brick from natural, indurated, diatomaceous earth deposits, such as Sil-O-Cel.

b. Fired mixtures of clay, diatomaceous earth, and cork scrap or sawdust for use in the insulation of boilers and furnaces. (Nonpareil.)

[1] 1, C9–17. "Standard Specifications and Tests for Portland Cement, Amer. Soc. for Testing Materials (1917).

CHAPTER II

FORMATION OF CLAY

A. INTRODUCTION

Definition of Clay.—Nature is engaged in the disintegration of the igneous rocks, the transportation, classification, and deposition of the products of disintegration and the recombination of these loose sediments, by heat, pressure, chemical activity, or crystallization, into dense masses, which often resemble the original igneous rocks. Clays are found among the sediments in the intermediate stage. They must not contain too great a quantity of the unaltered igneous rocks or of the rehardened metamorphic[1] rocks. To be classified as clay material, the proportion of the hard to the softened ingredients is commonly limited by the usefulness of the material for maufacturing clay products.

Clays are the weathered products of the silicate rocks, containing sufficient hydrous silicate of alumina in the softened condition to produce a plastic or semiplastic mass when tempered with water.[2] Some clays, such as the flint clays and hard shales, have been so hardened by pressure, heat, or the setting of their colloidal constituents that severe tempering processes must be employed to reseparate the fine particles and permit the penetration of water into the mass.

[1] In the broader sense *metamorphism* "covers all chemical and physical changes in rocks subsequent to their primary crystallization from magma." *Katamorphism* is the destructive division (weathering) and *anamorphism* is the constructive division.

Leith, C. K., and W. J. Mead: "Metamorphic Geology," p. xvii, Henry Holt and Company (1915).

[2] Other definitions of clay:

1. Orton, Jr., Edward: Lecture notes, Ohio State University.
2. Mellor, J. W.: "Clay and Pottery Industries," **1**, 158 (1914).
3. Ries, H.: "Clays, Occurrence, Properties and Uses," **1**, (1908).

Hence, each clay contains evidence of its geological history: its parent igneous rock; the mechanical and chemical disintegration of past ages; the leaching out of soluble salts and the infiltration of other salts; the transportation by water, wind, or ice and subsequent sedimentation in stream channels and quiet lakes or coagulation in the saline waters of the ocean; the addition of vegetable and other organic matter from growing things; the pressure of overlying strata or crustal movements of the earth; possible heat from volcanic activity; alteration from steam and other gases; and metamorphic changes from chemical hardening or colloidal setting.

B. GEOPHYSICAL-CHEMICAL RELATIONSHIPS

1. Silicic Acids and Silicates

Since the essential and characteristic ingredient of clay is an aluminum salt of a silicic acid, some of the knowledge of these acids should be reviewed.

Although it has never been isolated, the normal silicic acid (orthosilicic) would have the composition $Si(OH)_4$ or $SiO_2 2H_2O$. Many silicates corresponding to this acid are found in nature, for example, forsterite, $2MgOSiO_2$, and fayalite, $2FeOSiO_2$. The metasilicic acid, SiO_2-H_2O, is also unknown, but wollastonite, $CaOSiO_2$, enstatite, $MgOSiO_2$, and sillimanite, andalusite, or cyanite, $Al_2O_3SiO_2$, are examples of the corresponding silicates. The possible number of such mineral combinations is probably very great, for we have crystalline kaolinite, $Al_2O_3 2SiO_2 2H_2O$, and crystalline mullite, the only high-temperature aluminum silicate known with the 3:2 ratio, $3Al_2O_3 2SiO_2$. The so-called "silicic acids" are not definite forms and the common silicic acid gels (hydrated forms of silica) should therefore be given the general formula, $XSiO_2YH_2O$, in which the quantity of water can vary from 98 to but a few per cent.

The common silicates are combinations of a limited number of relatively simple compounds: silica, alu-

mina, iron oxide, calcium oxide, magnesium oxide, and the alkalies. A familiar example of a more complex combination is found in the feldspar group, ranging from orthoclase (microcline) and albite to anorthite or from $\left.\begin{matrix}K_2O \\ Na_2O\end{matrix}\right\} Al_2O_3 6SiO_2$ to $CaOAl_2O_32SiO_2$. Mixtures are found in nature which contain any proportion of these three forms. Complexity is a common characteristic of most silicates.

Solubility of Silicates.—Most of the common natural silicates, being the end products of geochemical reactions, are comparatively insoluble in ordinary solvents, and hydrofluoric is the only acid which attacks them easily at ordinary temperatures. The hydrous aluminum silicate or basic ingredient of most clays will dissolve slowly in hot concentrated sulphuric acid. A large number of the alkali silicates are soluble. The easiest method, therefore, of converting the ordinary silicate into a water soluble or common acid soluble form is to fuse it with an alkali such as sodium carbonate. This is the method employed for the ordinary chemical analysis. In ceramic work, however, primary interest is in the reactions between the different silicates themselves to form new combinations which produce certain physical properties such as strength, hardness, increased density, dielectric strength, non-absorption, etc. Interest is usually concerned with the production of new silicate compounds which will resist solution by water, dissolved salts, and acids, and in some cases the attack of molten slags, glasses, and high-temperature gases. The field of the water-soluble silicates such as sodium silicate or water glass is commonly left to the field of general chemical engineering.

Pyrochemical Reactions of Silicates.—The usual chemical reaction takes place between the dispersed ions of salts in water. In a similar manner, the reactions between silicates may be regarded as proceeding in high temperature or molten liquids in which the various components are dispersed as ions and can combine according to their natural affinities under the proper conditions. The viscos-

ity of these fluid silicates, however, is usually great or becomes so by slight reductions in temperature. The molecular movement in the liquid is therefore retarded, and definite crystalline forms or solid amorphous forms are produced with difficulty in artificial melts. Pure salts can be separated from aqueous solutions by evaporation of the liquid, or settling, filtering, and washing of the salt, processes which are impossible in the usual high-temperature, artificial silicate solutions. In metallurgy, the difference in specific gravity will permit the metallic portion of a melt to settle to the bottom of the molten bath and the lighter silicate (slag) can be skimmed off the surface. Ferrosilicon can be settled in a bath of mullite which has been melted in the electric furnace.[1] Many natural silicate salts slowly form and separate, in some cases, into enormous and comparatively pure masses because of slight differences in specific gravity in the natural silicate magmas, which have remained for long periods of time at high temperatures in the fluid condition in deeply buried batholiths. It must be remembered, however, that the usual silicate reaction which takes place in a vitrified ceramic body is necessarily incomplete, due to the short length of time and the low temperature. To carry the reaction to completion means the production of a fluid glass of the entire mass and the destruction of the shape of the article fired. The strength produced has been developed by the formation and chilling of a fluid formed only by the most easily softened ingredients. More and more crystalline silicates are being discovered and produced artificially. Yet one of the most common characteristics of silicates is that of preserving the vitreous or glass-like condition. This is especially true of those silicates having a high silica content. Among the lower silica silicates there is one which is unique in its ability to crystallize readily. Mullite, $3Al_2O_32SiO_2$, will develop in all types of vitrified ceramic bodies of the proper composition and

[1] Wilson, Sims, and Schroeder: "Artificial Sillimanite," *J. Am. Ceram. Soc.*, **7**, 847 (1924).

from molten liquids even when chilled by quenching. For more data on high-temperature silicate reactions, see Chaps. VI and VII.

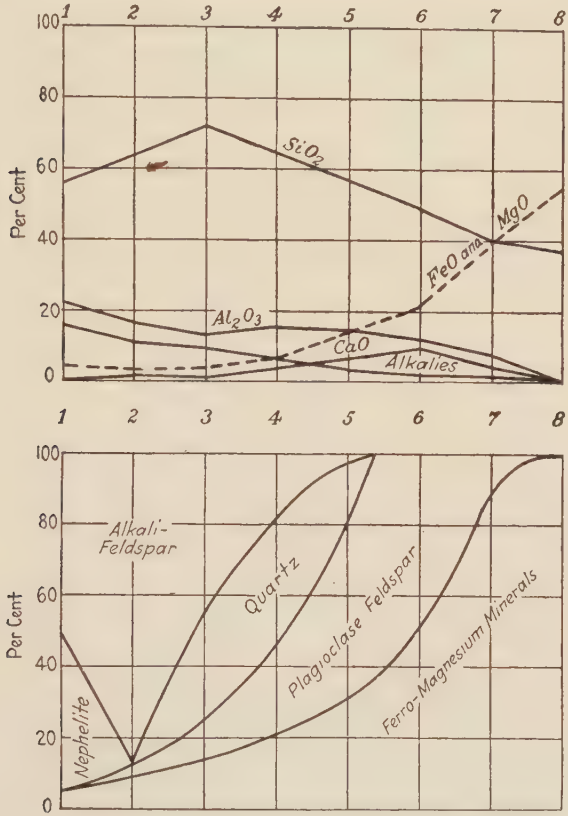


FIG. 1.—General chemical and mineralogical composition of igneous rocks. (*Pirsson, Rocks and Rock Minerals*, 144–145 (1915).)

	PLUTONIC ROCKS	VOLCANIC EQUIVALENTS
1.	Nephelite syenite	Phonolite
2.	Syenite	Trachyte
3.	Granite	Rhyolite
4.	Quartz diorite	Dacite
5.	Diorite	Andesite
6.	Gabbro	Basalt
7.	Peridotite	Basalt
8.	Dunite	Basalt

Composition of Common Igneous Rocks.—The upper chart of Fig. 1 shows the oxide and the lower chart the mineral composition of the common igneous rocks from

which the bulk of the clays are derived. As these individuals can be again grouped into two large classes of rocks, granites, and basalts, some idea of the average compositions of mixtures of the rocks can be gained from the average analyses of the two groups and when combined as 65 per cent of granite to 35 per cent of basalt, which is the proportion of occurrence (see Table III).

TABLE III.—CHEMICAL ANALYSIS OF THE AVERAGE IGNEOUS ROCKS[1]

	Average granite	Average basalt	Granite—65, basalt—35
SiO_2	70.47	49.65	63.18
Al_2O_3	14.90	16.13	15.35
Fe_2O_3	1.63	5.47	2.97
FeO	1.68	6.45	3.35
MgO	0.98	6.14	2.79
CaO	2.17	9.07	4.58
Na_2O	3.31	3.24	3.28
K_2O	4.10	1.66	3.24
TiO_2	0.39	1.41	
P_2O_5	0.24	0.48	
	99.87	99.70	

[1] LEITH, C. K., and W. J. MEAD: "Metamorphic Geology," p. 71, Henry Holt & Company (1915).

2. GENERAL WEATHERING AND ALTERATION AGENCIES

Clay is the product of rock destruction by weathering agents. As a molten rock or magma enters the outer shell of the earth and hardens by cooling, weathering agencies begin their attack. Water, carbon dioxide, and oxygen are the common agents which produce the chemical changes. The ferrous iron of the igneous rock combines with oxygen and water and a large portion remains as residual limonite. Alkalies and alkaline earths are dissolved and removed in a well-determined order. The remainder of the bases, not leached out, tend to remain combined with alumina and silica, taking on water and forming new hydrous silicates. Free quartz is the most resistant to change and solution. The remaining mass then

consists of a variety of hydrous aluminum silicates, quartz, iron oxide, and small amounts of soluble materials. When this has softened so that plasticity has developed, it is called clay.[1]

WEATHERING AGENCIES

I. Mechanical changes or disintegration
   A. Erosion and denudation
      Water, wind, and ice
   B. Temperature
      Freezing water, heat and cold
   C. Plants and animals
II. Chemical changes or decompositions
   A. Oxidation
   B. Hydration and dehydration
   C. Solution
      Water, pure or acidulated
      Pneumatolytic action of hot gases and liquids
   D. Deoxidation

3. Relative Solubility of the Common Igneous Minerals When Exposed to Similar Weathering Conditions[2]

Table IV

Easily soluble	Less soluble	Practically insoluble
1. Pyroxenes, CaO (Mg, Fe)O2SiO_2	1. Biotite, (H,K)$_2$O-2 (M g, F e) O Al_2O_3-3SiO_2	1. Quartz, SiO_2
2. Amphiboles, CaO-3(Mg, Fe)O4SiO_2	2. Feldspathoids, leucite, $K_2OAl_2O_34SiO_2$	2. Muscovite, K_2O3Al_2-$O_36SiO_2H_2O$
3. Olivine, 2(Mg, Fe)O-SiO_2	3. Plagioclase feldspars Anorthite, CaO Al_2O_3-2SiO_2	3. Zircon, ZrO_2SiO_2
4. Pyrite, FeS_2	Albite, $Na_2OAl_2O_3$-6SiO_2	4. Corundum, Al_2O_3
5. Apatite, $Ca_4(PO_4)_3$-(CaF)	4. Alkalic feldspars Orthoclase, K_2OAl_2-O_36SiO_2	5. Chromite, $FeOCr_2O_3$
		6. Ilmenite, $FeOTiO_2$
		7. Hematite, Fe_2O_3

[1] See Leith, C. K., and W. J.: Mead, "Metamorphic Geology," Henry Holt & Company (1915); Ernst, Weinschenk, "The Fundamental Principles of Petrology," McGraw-Hill Book Company, Inc., New York (1916).

[2] See Clarke, F. W.: "The Data of Geochemistry," *U. S. Geol. Survey, Bull.* 616, 481 (1916).

Laws of rock resistance:[1] (1) The more basic a rock becomes (except some of the ultrabasic) or the greater the quantity of sodium, potassium, magnesium, calcium, and iron, the more rapid the chemical decomposition. (2) Increase of alumina and silica causes less rapid decay.

TABLE V.—DECOMPOSITION OF GRANITE AND LAVA[1]

	Fresh Georgia granite	Decomposed granite	Gain or loss
SiO_2	68.75	38.50	−30.25
Al_2O_3	17.59	17.59	
Fe_2O_3	1.40	1.29	− 0.11
MgO	0.64	0.11	− 0.53
CaO	3.25	0.51	− 2.74
Na_2O	4.54	1.29	− 3.25
K_2O	3.27	1.63	− 1.64
H_2O	0.56	6.59	+ 6.03
	Fresh lava, Hawaiian	**Decomposed lava**	**Gain or loss**
SiO_2	52.45	5.82	−46.73
Al_2O_3	11.49	11.49	
Fe_2O_3	3.66	4.30	+ 0.64
FeO	6.90	0.91	− 5.99
Mn_2O_3	0.36	0.05	− 0.31
CaO	10.32	0.10	−10.22
MgO	5.81	0.06	− 5.75
Na_2O	2.44	0.08	− 2.36
K_2O	0.89	0.07	− 0.82
SO_3	0.20	0.22	+ 0.02
P_2O_5	0.38	0.07	− 0.31
TiO_2	4.07	1.36	− 2.71
H_2O	1.02	4.87	+ 3.79

[1] TWENHOFEL, W. H.: "Treatise on Sedimentation," Williams and Wilkins Company, Baltimore, 1926.

WATSON, T. L.: "Granites and Gneisses of Georgia," *Georgia Geol. Survey Bull.* 9-*A*, 312, 325–327 (1902).

[1] BUCKMAN, H. O.: "The Chemical and Physical Processes Involved in the Formation of Residual Clay," *Trans. Am. Ceram. Soc.*, **13,** 346 (1911); CUSHMAN, A. S.: "Rock Decomposition and Clay Formation," *Trans. Am. Ceram. Soc.*, **8,** 180 (1906).

4. Solution of Silicate Rocks and Diffusion through Rocks, Soils, and Clays (Ordinary Temperatures)

Mechanical disintegration greatly accelerates the chemical solution of our silicate rocks by exposing fresh surfaces for attack. The rate of chemical disintegration depends on: (1) The amount and character of the solvent (water with various dissolved gases and salts in this case), (2) the solubility of the original silicates and the products of solution, and (3) the removal of the products of solution. Once the chemical activity is under way, the rock mass can be divided into three classes:

1. The unaltered mineral grains *en masse* or ground to powder and ready for solution. These can be carried by gravity or mechanical means on the surface, but cannot pass through or diffuse through soils or rock masses.

2. The more easily diffusible portions of the solution, consisting of the soluble alkali salts, the soluble acid carbonates of calcium and magnesium, the slightly soluble ferrous compounds, the ferric humates, and the semicolloidal sodium and potassium silicates.

3. The less easily diffusible portions, consisting of the colloidal gelatinous silicic acid, the gelatinous hydrated silicates, and the colloidal hydrated ferric oxide.

Silicic acid is a very weak acid, and its salts, formed with the various bases from the common igneous rocks, are but minutely soluble in water. In geological time, however, this solubility is sufficient for complete solution or conversion into much simpler silicate forms. The salts of weak acids with strong bases hydrolyze when dissolved in water and form more or less ionized bases. In the case of the silicates there are the following:

1. The soluble hydroxides of sodium and potassium.
2. The less soluble hydroxides of calcium and magnesium.
3. The relatively insoluble hydroxide of iron.
4. Either the free un-ionized silicic acid or some simple alkaline silicates. If the products of the reaction are removed, simple silicates like kaolin or even free alumina and silica may be the final end products.

The dissolved materials will at the proper concentrations react with carbon dioxide of the soil or air to form the soluble and easily hydrolyzable carbonates of calcium and magnesium which may crystallize or form concretions. Ferrous silicates upon hydrolysis likewise give the slightly soluble ferrous hydroxide or carbonate or may oxidize to the ferric forms by dissolved oxygen present in the soils and precipitate as insoluble hydrated ferric oxide or basic carbonate.

Effect of the formation of secondary minerals. If an insoluble combination is formed from the dissolved salts, rock solution will be retarded. Chlorite,[1] serpentine,[2] and talc[3] are secondary minerals formed from magnesium-bearing rocks and are relatively stable in comparison with the corresponding lime silicates. Potassa may likewise produce a very stable form of white mica called "sericite,"[4] and the removal of potassium salts is further retarded because of their adsorption by colloidal clay. The potash feldspars are more resistant than the soda-lime or plagioclase feldspars and the secondary soda combinations are relatively soluble. Among the basic igneous rocks, chlorite, serpentine, and talc may be formed from augite and hornblende; chlorite and magnetite from biotite and serpentine; and magnetite from olivine.

Besides ionization and straight chemical reactions, it is necessary to consider the colloidal condition of the products of decomposition. (For a general introduction to the subject of colloids (see Chap. IV, p. 60). If the colloidal particles remain in the deflocculated or dispersed state, they can maintain their slow movements through the soil capillaries, and disintegration will proceed. If they are coagulated by adsorbing the oppositely charged ions of some salt, the disintegration is retarded. Once adsorbed, these salts are removed with varying degrees of ease. For

[1] Chlorite is the general name for the green silicates of aluminum with magnesium, ferrous iron, and hydroxyl.

[2] $3MgO2SiO_2H_2O$ with ferrous-iron impurities.

[3] $3MgO4SiO_2H_2O$ with ferrous-iron impurities.

[4] $K_2O3Al_2O_36SiO_2H_2O$.

instance, the adsorbed sodium salts can be washed out before the potassium and ammonium salts.

Alkaline soils tend to preserve the deflocculated condition and hence assist in the removal of the colloidal silicates and silicic acid, while the positively charged colloidal ferric hydroxide and aluminum hydroxide must remain until all alkalinity has disappeared before they can exist in suspension and be removed by leaching.

The colloidal silicates like clay do not assume a set gel condition on flocculation and drying, though there is a tendency in this direction. Kay and Pearce[1] suggest that the protective colloids of humic organic emulsoids formed from plant growth impart reversibility and stability to the silicate colloids, so that, after coagulation or even drying in the sun, they can again pass into suspension with the addition of water. Protective colloids from plant growth can be found with most clays, such as the shales, glacial, surface, and coal-measure clays, but for those deeply buried, residual kaolins, softened in place by alteration and pneumatolytic action, some other protection must be ascribed. It is true, however, in this case, that the disintegration has not proceeded so far, nor plasticity developed so well, as it has with those clays which have been exposed and moved around in contact with organic materials.

5. Pegmatite Dikes and Veins[2]

A large proportion of our commercial kaolin deposits have been derived from pegmatite dikes. Such dikes and veins are found in the plutonic or deeply buried, coarse-grained, igneous rocks of the granite family. These veins will often show a banded structure of the different minerals, feldspar, quartz, and mica, parallel to the walls of the intruded rock. As the original igneous mass cooled and crystallized, it shrank in volume and cracked. The

[1] Kay, G. F., and J. N. Pearce: "The Origin of Gumbotil," *J. Geol.*, **38** (2) (1920).

[2] Ford, W. E.: "Dana's Manual of Mineralogy," pp. 345–348, John Wiley & Sons, Inc. (1912).

weight of the mass forced any remaining fluid up through these cracks and often into fissures or planes of weakness in the surrounding rocks for great distances. As the main portion of the original mass crystallized, its content of vapors and gases was forced into the last liquid, which consequently had a much higher concentration of these gases or was more "juicy" than the bulk of the igneous magma. This concentration of gases and vapors is of utmost importance in the kaolinization of the feldspar of the pegmatite dike. The presence of the gases, fluorine, boron, and hydroxyl, is shown by the accessory minerals found with both the unaltered and altered pegmatites. Some of the most common are:

Beryl	$3BeOAl_2O_36SiO_2$
Tourmaline	$R_9Al_3(B.OH)_2Si_4O_{19}$
Apatite	$Ca_4(CaF)(PO_4)_3$ or $3Ca_3P_2O_8.CaF_2$
Fluorite	CaF_2
Scapolite	isomorphic mixture of $4CaO3Al_2O_36SiO_2$ and $Na_4Al_3Si_9O_{24}Cl$
Topaz	$(Al(F.OH))_2SiO_4$
Chondrodite	$Mg_3(Mg(F.OH))_2(SiO_4)_2$

6. Kaolinization

Two different, yet related processes have been noted in the production of kaolin from feldspar. In the first, endomorphic alteration has disintegrated the feldspar at depth, independent of the atmospheric weathering agencies. In the second, the disintegration process is due to the normal chemical agencies present on the surface. Alteration at depth is intense and complete within the sphere of the gas and vapor action mentioned in the preceding paragraph. The feldspar is subjected to concentrated, high-temperature attack of fluorine, boron, steam, and possibly other gases under high pressure. Since the action takes place at great depths, the semikaolinized feldspar formed is not exposed to erosion and removal as fast as the crystalline mass has softened, as is often the case in weathering processes at the surface.[1]

[1] Weinschenk, Ernst: "The Fundamental Principles of Petrology," pp. 73, 78, 143, 149, McGraw-Hill Book Company, Inc., New York (1916).

Partial alteration or kaolinization of feldspar crystals is commonly observed at depths in feldspar deposits which could not have been reached by percolating waters or other atmospheric agencies. Alteration produces very irregular, isolated masses of kaolin often surrounded by unaltered feldspar. Atmospheric agencies produce regional changes. The irregularity of the former type can be explained by the fact that some portions of the original molten mass were more "juicy" than others and that in some places the gases escaped more readily. A shrinkage crack or fault in the Cornwall deposit has apparently permitted the escape of gases from one side and not from the other.[1] Biotite, $(H, K)_2O2(Mg, Fe)OAl_2O_33SiO_2$, is one of the first minerals to be affected by surface weathering, but is often found fresh in altered kaolins.[2] The depth of alteration is much greater than that which can be obtained by surface agencies. Kaolin is found 500 feet below the surface, and some of the richest kaolin is found at the greater depths. The Cornwall beds in England are capped by a disintegrated but unaltered granite layer at the surface, from 4 to 14 feet thick, which under normal weathering would have been the first to kaolinize. Kaolinization by pneumatolytic action of gases and vapors can be noted in progress at the present time near the kaolin deposits at the hot springs of Karlsbad, Bohemia, and the relationship is apparent. Besides the kaolin beds of Cornwall, England, and Karlsbad, Bohemia, another series is found near Spokane, Wash., which was undoubtedly formed by endomorphic alteration and not by weathering.[3]

The production of kaolin is the Appalachian district of Georgia, the Carolinas, and Virginia, however, is apparently due to surface weathering. Watts[4] notes the following in his description of these deposits:

[1] Leech, Stephen: "China Clay," *Bull. Am. Ceram. Soc.*, **4**, 639 (1925).

[2] Weinschenk, Ernst: "The Fundamental Principles of Petrology," pp. 73, 78, 143, 149, McGraw-Hill Book Company, Inc., New York (1916).

[3] Goodspeed, G. E.: "Formation of Kaolin at Freeman Washington," *U. S. Bur. Mines Rept. of Investigation* (1927).

[4] Watts, A. S.: "Kaolin Mining in the South Appalachian Mountains," *Trans. Am. Ceram. Soc.*, **14** (1912).

1. The extent of kaolinization varies inversely with the depth.

2. Unplastic, semikaolinized feldspar is found at depths of 40 to 45 feet.

3. The richest and most plastic kaolin is found at about the present water level.

On the other hand, fresh feldspar and completely kaolinized feldspar are to be found almost side by side at the same elevation. The accessory minerals found in the kaolin or near by are garnet,[1] biotite, tourmaline, beryl, and cassiterite, SnO_2. The only possible theory to account for this kaolinization in terms of the alteration theory is that, after alteration at depth, the upper portions of the kaolin together with the surrounding country rock were removed by weathering until at the present time semikaolinized material is reached at 40 to 45 feet below the surface. Contrary evidence undoubtedly makes this theory untenable.

Chemical Changes in the Kaolinization of Potash Feldspar. The accompanying chart (Fig. 2) represents the theoretical kaolinization of potash feldspar, the washing of the original kaolin to produce the commercial washed china clay, and the relative composition and refractoriness of the more common types of clay. In a similar manner, soda and lime feldspars and other aluminum silicates produce more or less pure forms of clay matter as they weather and soften. In most cases, the end product is one of the impure types of clay.

Pure potash feldspar is represented by the molecular formula

$$K_2OAl_2O_36SiO_2$$

and deforms near cone 8 or approximately 1200° C. From the molecular standpoint the kaolinization is as follows:

$$K_2OAl_2O_36SiO_2 + \text{weathering} + 2H_2O + CO_2 = Al_2O_32SiO_22H_2O + 4SiO_2 + K_2CO_3.$$

[1] Garnet. $R_3'' R_2''' (SiO_4)_3$ where the R'' may be calcium, magnesium, ferrous iron, and manganese and the R''' may be aluminum, ferric iron or chromium.

The soluble potash salts are partially removed by percolating waters, while the four molecules of silica may diffuse as colloidal silicic acid or coagulate to an

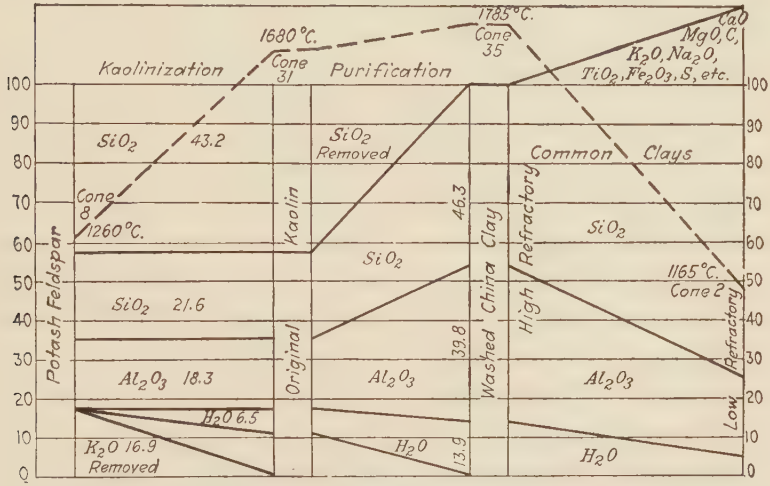


FIG. 2.—Kaolinization of potash feldspar, the washing of the residual kaolin and the relative composition and refractoriness of mixed clays.

amorphous set gel condition. Considered from a percentage basis:

Potash Feldspar			Kaolin Deposit			Washed China Clay
SiO_2	64.8		silica	$43.2SiO_2$		
Al_2O_3	18.3	+ weathering =	kaolin	$21.6SiO_2$	+ washing =	$46.3SiO_2$
K_2O	16.9			$18.3Al_2O_3$		$39.8Al_2O_3$
				$6.5H_2O$		$13.9H_2O$
	100.0			89.6		100.0

As kaolinization proceeds and the alkali is removed, the refractoriness is increased to a maximum of cone 31 (1680° C.) with the quartz remaining. When the quartz has been removed, the theoretical cone fusion point of the washed china clay is cone 35 (1785° C.). The admixture with other fluxes, such as lime, magnesia iron, and the alkalies, may cause the fusion point to drop as low as cone 2 or about 1165° C. The right side of Fig. 2, then, represents the varying composition of common clays. Figure 2 does not imply that the impure clays are all formed by mixing pure kaolin formed from potash feldspar

with impurities. In the decomposition of a basalt or similar highly basic rock a hydrated aluminum silicate having a composition similar to that of kaolin is formed, called the clay substance of the mass, but its composition may be entirely unlike that of kaolin and more like one of the hydrous silicates given in the following table by Clarke. Likewise, the associated basic minerals of the basalt are decomposing at the same time as the feldspars. Their decomposition products are at all times inseparable from the aluminum silicates. Muscovite and sericite also weather to form kaolin.

According to Frank W. Clarke, a few of the following silicates are definite compounds, others have doubtful compositions, and some are probably only colloidal mixtures:

TABLE VI.—HYDROUS SILICATES OF ALUMINA[1]

Kaolinite	$H_4Al_2Si_2O_9$	$1Al_2O_3 2SiO_2 2H_2O$
Halloysite	$H_4Al_2Si_2O_9$ plus aq.	$1Al_2O_3 2SiO_2 2H_2O$ plus aq.
Newtonite	$H_8Al_2Si_2O_{11}$ plus aq.	$1Al_2O_3 2SiO_2 4H_2O$ plus aq.
Cimolite	$H_6Al_4Si_9O_{27}$ plus 3 aq.	$2Al_2O_3 9SiO_2 3H_2O$ plus 3 aq.
Montmorillonite	$H_2Al_2Si_4O_{12}$ plus n aq.	$1Al_2O_3 4SiO_2 1H_2O$ plus n aq.
Pyrophyllite[a]	$H_2Al_2Si_4O_{12}$	$1Al_2O_3 4SiO_2 1H_2O$
Allophane	Al_2SiO_5 5 aq.	$1Al_2O_3 1SiO_2 5H_2O$
Collyrite	Al_4SiO_8 9 aq.	$2Al_2O_3 1SiO_2 9H_2O$
Schrotterite	$Al_{16}Si_3O_{30}$ 30 aq.	$8Al_2O_3 3SiO_2 30H_2O$

[1] CLARKE FRANK W.: The Data of Geochemistey," *U. S. Geol. Survey, Bull.* 616, 610-611 (1916).

[a] BURGER, O. K.: "Agalmatolith, a New Refractory Material," *J. Am. Ceram. Soc.*, **9**, 343 (1926).

7. LATERIZATION

In the majority of cases, the decomposition end products of the original complex aluminum silicates are the colloidal hydrated aluminum silicates. In many cases, however, where the volume of seasonal advance and recession of ground water is large or where an open texture of the soil is maintained for the free circulation of ground waters, there is a decomposition of the hydrated aluminum silicate to form hydrated alumina and hydrated silica. The

above conditions are more common in tropical or subtropical regions, where frost is not present to break down the open texture and where the soil is covered with a thick mantle of vegetation.[1] Laterization is also attributed to the work of microorganisms.[2] The original silicates may also decompose directly to form laterites. As the hydrated forms of silica[3] are soluble and therefore carried away faster than the hydrated forms of alumina and ferric oxides, the latter increase in concentration as the silica is removed. In special cases, such as found in Arkansas, Missouri, British Guiana, France, Ireland, and India, the concentration has been sufficient to form commercial beds of high-aluminous ores of gibbsite, $Al_2O_3 3H_2O$; bauxite, $Al_2O_3 2H_2O$; or diaspor, $Al_2O_3 1H_2O$.

$$Al_2O_3 2SiO_2 2H_2O + 2H_2O = Al_2O_3 2H_2O + 2(SiO_2 H_2O)$$

The bauxites find their chief service in the manufacture of metallic aluminum while the Missouri diaspor with its lower water content and lower shrinkage is mainly used for refractory wares. The hydrated oxides, therefore, represent the final end products of natural decomposition of the silicate rocks.

[1] Clarke, Frank W.: "The Data of Geochemistry," *U. S. Geol. Survey, Bull.* 616, 610–611 (1916); Twenhofel, W. H.: "Treatise on Sedimentation," p. 9, Williams and Wilkins Company, Baltimore (1926); Mead, W. J.: "Occurrence and Origin of the Bauxite Deposits of Arkansas," *Econ. Geol.*, **10,** 22–54 (1915); Leith, C. K. and W. J. Mead: "Metamorphic Geology," pp. 8, 25–37; Fermor, L. L.: "What Is Laterite," *Geol. Mag.*, Decade 5, **8,** 460 (1911).

[2] Holland, T. H.: "Origin and Dehydration of Laterite," *Geol. Mag.*, Decade 4, **10,** 49–69 (1903); Middleton, Jefferson: "Occurrence of High Alumina Clays," *U. S. Geol. Survey, Mineral Resources*, **1918,** II, 909–910 (1920); "Occurrence and Properties of Diaspor Clays of Missouri," *Missouri Bur. Mines* and *Geol. Biennial Rept.*, 17–20, State Geologist (1919); Wherry, E. T.: "Identification of Diasporite," *Am. Mineral.*, **3,** 154 (1918); Wysor, D. C.: "Diaspor Clays of Arkansas and Missouri," *J. Am. Ceram. Soc.*, **6,** 501 (1923).

[3] The silica liberated by the decomposition of silicates is far more soluble than are the ordinary quartz grains. Headdon treated orthoclase with water containing carbonic acid and obtained a solution, which when evaporated yielded a residue carrying over 40 per cent silica. Headdon, W. P.: "Significance of Silicic Acid in Waters of Mountain Streams," *Am. J. Sci.*, **16,** 180–181 (1903).

TABLE VII.—ANALYSES SHOWING FORMATION OF ARKANSAS BAUXITE FROM SYENITE[1]

	Unaltered nephelite syenite	Partially kaolinized syenite	Completely kaolinized syenite	Bauxite
SiO_2	58.00	52.64	39.80	10.64
Al_2O_3	27.10	29.56	37.74	57.48
Fe_2O_3	1.86	1.06	1.60	2.56
FeO	3.30	0.80	0.10	0.20
MgO	0.25			
CaO	1.62			
Na_2O	6.70	4.46		
K_2O	0.25	0.44		
TiO_2	0.40	1.20	3.30	1.20
H_2O	1.22	9.00	17.00	28.36
Total	100.70	99.16	99.54	100.44

[1] LEITH, C. K., and W. J. MEAD: "Metamorphic Geology," p. 30 (1915).

TABLE VIII.—AVERAGE ANALYSES OF IGNEOUS ROCKS AND SEDIMENTS[1]

	Average igneous rock	Average shale	Average sandstone	Average limestone
SiO_2	59.83	59.38	78.66	5.19
Al_2O_3	14.98	15.47	4.78	0.81
Fe_2O_3	2.65	4.03	1.08	0.54
FeO	3.46	2.46	0.30	
MgO	3.81	2.45	1.17	7.90
CaO	4.84	3.12	5.52	42.61
Na_2O	3.36	1.31	0.45	0.05
K_2O	2.99	3.25	1.32	0.33
H_2O^a +	1.42	3.68	1.33[b]	0.56[b]
TiO_2	0.78	0.65	0.25	0.06
CO_2	0.48	2.64	5.04	41.58
P_2O_5	0.29	0.17	0.08	0.04
$S + SO_3$	0.10	0.65	0.07	0.14
BaO	0.10	0.05	0.05	
MnO	0.10	Trace	Trace	0.05
C, organic	.....	0.81		
Totals	99.19	99.12	100.10	99.86

[1] CLARKE, FRANK: "Data Geochemistry," *U. S. Geol. Survey, Bull.* 616, 27, 28 (1916).
[a] H_2O above 110° C.
[b] Includes organic matter.

TABLE IX.—COMPARISON OF COMBINATION OF SEDIMENTS WITH AVERAGE IGNEOUS ROCK[1]

	Average shale	Average sandstone	Average limestone	Total sediments	Average igneous rock
SiO_2	51.70	10.150	0.348	62.198	60.20
Al_2O_3	13.71	0.615	0.054	14.379	15.05
Fe_2O_3	3.57	0.139	0.018	3.727	2.59
FeO	2.18	0.039	0.018	2.237	3.44
Fe	4.20	0.130	0.026	4.356	4.49
MgO	2.17	0.151	0.530	2.851	3.87
CaO	2.76	0.711	2.860	6.331	4.80
Na_2O	1.16	0.058	0.003	1.221	3.42
K_2O	2.88	0.170	0.022	3.072	3.01
H_2O +	3.26	0.172	0.038	3.470	1.48
TiO_2	0.58	0.032	0.004	0.616	0.74
P_2O_5	0.15	0.001	0.002	0.153	0.26
CO_2	2.34	0.649	2.793	5.782	0.48
SO_2	0.58	.....	0.003	0.583	0.28
C	0.72	.....	.....	0.72	
Total weights.....	91.96	13.017	6.719	111.696	104.11

[1] LEITH, C. K., and W. J. MEAD: "Metamorphic Geology," p. 80 (1915).

CHAPTER III

CHARACTERISTICS OF CLAY IN THE ORIGINAL CONDITION

A. CLASSIFICATION CHART OF THE PRINCIPAL TYPES OF CLAYS

The following outline gives a condensed and slightly revised form of a "Chart Showing the Principal Types of Clay Deposits and Their Relation to Each Other," by Prof. Edward Orton, Jr. Clays may be residual or transported. The residual or primary clays are those which, after their formation, have never been moved from the original parent rock. The transported or secondary clays have been moved and redeposited by the action of water, wind, or ice or combinations of the three. Red firing shales (group 12) form the great bulk of our clay material. A comparatively small amount has a sufficiently low content of iron salts to fire to a buff color, and only in isolated spots and in small deposits have the decomposition products of the pure feldspars been sufficiently protected from contaminating materials to enable them to fire white. Residual clays thus represent the decomposition product of a single rock or group of rocks, while transported clays usually represent the intermingling of sediments from the many rocks in a river system. The buff- and white-burning transported clays have either not been carried far or have only been moved over areas of similar rocks or over unweathered rock surfaces and have been deposited into small lakes or sheltered portions of larger waters. Primary clays usually contain unassorted particles varying from partially kaolinized, rotten rock fragments and the hard, unaltered, more resistant minerals, such as quartz, to the finest colloidal clay substance. On the other hand, transported clays have had the sorting action of wind or water to grade the sizes and to separate the plastic clay

material from the sand and gravel. Transported clays, therefore, as a class, present better commercial possibilities for a uniform production of raw material unless, as in the case of kaolin or china-clay production, the original material is to be purified.

TABLE X.—CHART OF PRINCIPAL TYPES OF CLAYS

Classification	Transportation	Color fired	Refractoriness	Original hardness	Common name	Uses
Primary or residual		Light	Medium or low	Rotten rock	1. Semikaolinized feldspar or granites; Cornish stone and Jap stone	Whiteware, white structural ware
	None	White	High	Soft	2. Residual kaolins; when washed produces china clay	Whiteware, refractories, paper, glazes
		Dark	Low	Soft	3. Residual basaltic clays, etc.	Common and face brick, drain and building tile
		Dark	Low	Soft	4. Aeolian primary clays, weathered volcanic ash	
Secondary or transported		White	High	Soft	5. Secondary kaolins (see Primary kaolins)	Whiteware, glazes, refractories; No. 5 for paper
		White	High	Soft	6. Ball clays	
		Buff	High	Hard	7. Flint fire clays	Refractories
		Buff	High	Soft	8. Bond clays	Refractories
	Water	Buff	High	Soft	9. Common fire clays	Refractories
		Buff	High	Soft	10. Aluminous allied minerals	Refractories
		Buff	Medium and low	Soft	11. Poor refractory clays, terra cotta, stoneware, etc.	Pottery, structural, art pottery, etc.
		Dark	Low	Hard	12. Siliceous shales Calcareous shales Ferruginous shales Carbonaceous shales	Structural, brick, and tile
		Dark	Low	Soft	13. Bedded clays	Structural
		Dark	Low	Soft	14. Alluvial clays	Brick and tile
	Wind	Dark	Low	Soft	15. Weathered loess	Structural, brick and tile
	Ice	Dark	Low	Soft	16. Glacial lake clays (sorted by water)	Structural brick and tile, flower pots
	Ice	Dark	Low	Soft	17. Weathered glacial till	

[1] Condensed from chart of Edward Orton, Jr.

B. DESCRIPTIONS OF CLAYS

1. SEMIKAOLINIZED FELDSPAR OR GRANITE

This represents an intermediate phase in the decomposition of feldspar. A portion of the alkali remains, the combined water content is low, and plasticity is absent or

but partially developed. Examples: Cornwall stone of England, Japanese native rock, semikaolinized feldspar from Georgia and rotten rhyolite from Taylor, Wash. Some of these bodies are similar in composition, and vitrifying properties to a weakly plastic synthetic porcelain body, containing feldspar, china clay, and quartz. Light-colored face brick have been made in Washington and in Georgia from these materials. Cornwall stone has been used for generations as a weak flux in pottery bodies and glazes all over the world. The Japanese use their native materials for gray-colored pottery bodies of the cheaper grades.

2. Residual Kaolins

The final products of the kaolinization of alkali feldspars and allied minerals which have decayed in place without movement. The alkali content is at a minimum, and at least feeble plasticity has been developed. The white or cream-colored clay material is usually associated with unaltered quartz and mica. Such material is now used for a cone 31 siliceous fire clay. When purified, the china clay is very valuable for whiteware pottery, tile, paper filler, and glazes. The refractoriness has been raised to near cone 34. Theoretically it should be cone 35 for the purest types of kaolin. The residual kaolins are usually coarser grained and have less plasticity than the transported kaolins. Examples: the English kaolins from Cornwall, the North Carolina kaolins, and the plastic residual or colluvial kaolins from eastern Washington and northwestern Idaho.

Definitions of China Clay, China-clay Rock, Kaolin, Kaolinite, and Clay Substance.[1]—*Kaolinite* is the mineral form of $Al_2O_32SiO_22H_2O$, having a definite crystalline form and a definite composition. It occurs in small quantities as microscopic crystals in the purer clays, but

[1] Mellor, J. W.: "Clay and Pottery Industry," **1**, 166 (1914). Mellor suggests the word *clayite* for the "hydrated aluminum silicate which occurs in most clays in non-crystalline or amorphous granules and corresponds to the formula $Al_2O_32SiO_22H_2O$."

is non-plastic, and the crystals are usually badly worn and rounded.

Kaolin is the amorphous variety of $Al_2O_32SiO_22H_2O$, or the most important and abundant constituent of china clay. The central portions of some of the larger grains of kaolin have been found to be the crystalline kaolinite. Kaolin is not necessarily the decomposition product of kaolinite, however. Kaolin is also used as a general term including both china clay and china-clay rock. For instance, the prepared china clay from Florida is still called "Florida kaolin" in commercial circles.

China clay is the comparatively pure commercial variety of kaolin which has been derived from the china-clay or kaolin rock by natural or artificial elutriation, levigation, and sedimentation.

China-clay rock (*kaolin rock*) is the altered or weathered mixture consisting of kaolin, quartz, mica, and other accessory minerals as found in nature.

Clay substance is the general term for the plastic hydrous aluminum silicate of indefinite composition found in all types of clay. For the benefit of normative calculation, it is regarded as $Al_2O_32SiO_22H_2O$. The clay substance is also regarded as that portion of a clay mass which is soluble by digestion in hot concentrated sulphuric acid in the so-called rational analysis.

3. Residual Basaltic Clays

These are red burning clays which have been formed in place by the weathering of basalt rock. They are used for the common structural wares. The largest basalt flows of the world are found in eastern Washington and Oregon where hundreds of cubic miles of basalt emerged in successive flows. A large part of the decomposition products have been removed by the wind.

4. Aeolian Primary Clays—Weathered Volcanic Ash

Volcanic ash is the material of variable composition which has been blown from volcanos by explosive action.

Because of the rapid cooling, the individual microscopic particles are originally small fragments of glass bubbles. As a mass the ash is usually a light-weight, light-gray material which is often mistaken for diatomaceous earth or china clay. It can be distinguished by a microscopic examination or by heating. Most ashes will fuse to a black glass between cones 02 and 6. Because of the great surface exposed to percolating waters and the amorphous condition, the ash weathers very rapidly in damp climates and forms either red- or buff-burning clays of great plasticity and high shrinkage. Some bentonite is also derived from volcanic ash.[1] Most of these materials are unfit for fired ceramic wares alone, but can be used in small quantities with other weakly plastic, synthetic bodies to improve the plastic working strength. After an eruption, volcanic ash will be picked up by streams, transported, and deposited in stratified beds. Large accumulations of both the weathered and unweathered volcanic ash are found among the foothills of the Pacific Coast mountain ranges in the old volcanic regions of Washington, Oregon, and California.

5. Secondary Kaolins

These are kaolins which have been transported short distances by streams and deposited in lakes or sheltered arms of the ocean. Some deposits are too badly stained for whiteware purposes, but have a high refractory value, while others are mixed with semikaolinized feldspar or other cheap fluxes for cream-colored structural wares.[2] Some of the Georgia beds contain as high as 99 per cent clay material, while those of Florida yield as low as 25 per cent kaolin on purification. The kaolin strata are interbedded with other sedimentary materials such as sands and even limestone. Most of the secondary kaolins are finer grained and have their plasticity developed to a

[1] Ross, C. S., and E. V. Shamon: "The Minerals of Bentonite," *J. Am. Ceram. Soc.* **9**, 77 (1926).

[2] Staff Article, *The Ceramist*, **8** (2) 114 (May, 1926).

higher degree than the residual kaolins, but do not have the bonding strength of ball clays.

6. Ball Clays

The white- or light-cream-burning clays which represent the maximum degree of subdivision and the highest degree of plasticity of the fired clay materials are called "ball clays." They are dug from the deposits in large, tough, ball-shaped masses and shipped without purification. The material represents the finest of the pure clay substance which will float the longest time in quiet lakes. Ball clay-like material can be separated to a slight extent by artificial elutriation from china clays. They are often dark gray in color and sometimes black from the association with vegetation in shallow, swamp-like lakes. They are similar to the secondary kaolins, but show greater toughness, more bonding power in the plastic condition, vitrify to dense impervious bodies at comparatively low temperatures (cones 6–8), and maintain this condition until high temperatures, without bloating or developing a vesicular condition. The china clays vitrify at higher temperatures, have higher softening temperatures, and represent purer, less contaminated clay substance. Examples: the ball clays of Dorsetshire, England, southwestern Kentucky, and Tennessee.

7. Flint Fire Clays

A hard, dense, high-aluminous, flint-like (not high in silica content) clay material which in the original condition breaks with a conchoidal fracture. The plasticity is very low with the ordinary tempering methods, but may be partially restored by ball-mill or wet-pan grinding in water. Flint fire clays are similar to ball clays in composition, color, and firing properties, but represent a hardened or set gel condition of what was formerly very finely divided, plastic clay substance. Some types are richer in alumina than kaolin and thus represent a certain degree of laterization. Like ball clays they have high-fired shrink-

age and crack badly. Until the use of kaolin fire clays, the flint fire clays, bonded with more plastic fire clays, formed the most refractory commercial fire clays. Examples: flint fire clays are found at Olive Hill, Ky., interstratified with plastic No. 2 fire clays; in Missouri limestone pockets; and at Kummer, Wash., interbedded with red-burning shales, coal, and sandstone seams.

8. Refractory Bond Clays

The ball clays are bond or bonding clays in that they are used to provide plastic and fired strength to various non-plastic or weakly plastic materials. The refractory bond clays are those whose special properties of plasticity or long range of vitrification have made them valuable in the manufacture of glass refractories, graphite crucibles, and similar products. They usually burn to darker colors than the ball clays which have been found valuable for whiteware, and some bond clays have rather high silica contents. They were formerly imported to America in large quantities from Gros Almerode and Klingenberg, Germany, and from England, but these have now been mostly replaced by combinations of clays from Kentucky, southern Illinois, Arkansas, and Missouri.

9. Common Fire Clays

Buff- or light-brown-firing clays which have softening points of at least equal to cone 19 and which can be used for some type of refractory clay service are found in nearly all parts of the world. Many are used for structural wares as in No.11.

10. Aluminous Allied Materials

When the alumina content exceeds that of pure kaolin (39.8 per cent) some form of alumina hydrate is probably present. Bauxite is used mainly as a source of aluminum metal and comes from Arkansas, Georgia, British Guiana, India, France, and Ireland. The more impure forms are used for refractories and in the electric furnace production of

crystalline corundum, which serves both as an abrasive and refractory. The diaspors of east central Missouri, however, are now extensively used for a superior type of fire brick similar in type but more refractory than the ordinary fire clays.

11. Low-refractory, Buff-firing Clays

In general, buff-burning clays represent a more refractory type than the dark- or red-burning clays, but numerous exceptions may be found. Some form of iron oxide is the cause of the red or dark color and it alone may not be a very active flux. But when a clay contains enough iron to fire dark, it usually represents one of the impure types containing sufficient quantities of the other fluxes to cause a low temperature of softening. On the other hand, a buff-burning clay may contain a high quantity of alkali or lime and yet insufficient iron to fire dark. Clays from Kelso, Wash., and Willamina, Ore., are of this nature. The usual impurities in the low-refractory, buff-burning clays are excess quartz, feldspar, and mica with small quantities of lime, magnesia, and iron oxide. Large quantities of these clays occur in the coal-bearing formations of eastern Ohio and Pennsylvania. They may have a uniform extent of considerable area as distinct seams or may occur in small, lens-shaped beds of limited quantity. The hardness will vary from the hard, massive, shale-like variety without much pronounced fissle structure to the soft, cheese-like types, which have never been subjected to pressure. Such are found all over the United States. They give their greatest service for the buff-burning structural brick and tile of the lighter colored varieties, for architectural terra cotta, and various forms of pottery, such as stoneware, yellow bowls, or even the bodies for some of the best art pottery.

12. Shales

Shales are moderately hard clay strata which have been compressed and often heated, but not to the point of chemical alteration. Fissle structure is usually present, but not

perfect enough to split like slate. Shales soften and become more clay like on exposure to weather. They are often but feebly plastic when first mixed with water, but recover their plasticity by continued grinding, preferably in water. Most shales fire to red or brown colors, a few are buff burning, and one at least from Williams Lake in British Columbia fires to a near-white color. Under the influence of pressure, a portion of the water has been expelled so that the resulting shale is much less hydrous. In comparing the analyses of shales with similar soft clays, the most noticeable feature is the change in the iron oxide.[1] The proportion of ferrous to ferric oxide has increased in the shale. This is probably due to the long-continued reducing action of the organic matter in the original sediments. If the pressure is continued, the shales become more compact, less hydrous and change into clay slates. By further metamorphism, the slates are transformed into metamorphic schists in which various new minerals appear. Shales form the basis of an enormous clay industry.

Fissle Structure of Shales.—Tyndall[2] showed that a laminated structure is produced if an apparently homogeneous mass is subjected to pressure under such conditions that it can yield at right angles to the pressure. Even pure-white wax when chilled and compressed can be split into laminae of extraordinary thinness. This action is similar to the development of lamination in a column of clay as it is pushed through a die in a brick or tile machine. Mica particles will arrange themselves perpendicular to the applied pressure, and in a similar manner any irregular-shaped clay or sand grain will orient itself to present its broadest surface perpendicular to the pressure. Separation then becomes easiest along parallel planes.

a. Siliceous Shales.—This is the most common variety of all the shales, and all degrees of sandiness from the plas-

[1] CLARKE, F. W.: "Data of Geochemistry," *U. S. Geol. Survey, Bull.* 616, 546 (1916).

[2] TYNDALL: "Fragments of Science: On Crystalline and Slaty Cleavage;" BECKER: *U. S. Geol. Survey, Bull.* 241 (1904).

tic, clay-like shales to sandstones may be obtained. Examples: common shale material in the middle-western part of the United States or the Tertiary shales on the ocean slopes of the Cascade Mountains in Oregon and Washington.

b. Calcareous Shales.—Containing carbonate or sulphate of lime from a few per cent to high amounts, so that the material approaches limestone or gypsum in composition. Clays containing more than 4 or 5 per cent $CaCO_3$ or appreciable amounts of calcium sulphate are of little value for clay products. Some may be used in portland cement mixtures.

c. Ferruginous Shales.—The iron content of red-burning clays usually lies between 4 and 7 per cent ferric oxide. This may be increased by organic, mechanical, or chemical concentration until the clay is classed as an iron ore. Examples: low-grade iron ores near Nooksack, Wash., bog iron-ore capping of clays in eastern Washington, and iron ores near Portland, Ore.

d. Carbonaceous Shales.—If clay sediments are deposited in swamps among growing vegetation and no subsequent oxidation period prevails, the later clay or shale deposit will be darkened by carbon. As the carbon content increases, the shale approaches the character of bone coal. The carbon content of clays may be leaves, wood, peat, lignite, bituminous or anthracite coal matter, graphite, or asphalt. Small quantities of the more easily combustible forms are not harmful, but large quantities of the more difficultly burning forms require too much time for removal in the kiln firing and prevent the oxidization of the other constituents before vitrification. Examples of carbonaceous shales may be found in the Huron and Bedford shales of Ohio and those occurring with the Eocene measures of western Washington.

13. Bedded Clays

This is a term applied to soft clays which have not been hardened into the shale type but show distinct lamination planes due to irregularities in their deposition. They can be worked with ease, disintegrate readily in water, and

behave like young or soft shales. Bedded clays may originate as alluvial clays, glacial-lake clays, etc. Concretionary growths have not had time to form. Shales which have weathered in place after being exposed on the surface form bedded clays.

14. Alluvial Clays

Alluvial clays are those flood-plain clays which have been recently deposited along present drainage channels and consist of soft, unconsolidated material with little or no fissle structure. They are plastic and easily worked and often give a wide variety of fired colors for the darker-colored face brick. Examples are found at Groveport and Fredericksburg, Ohio.

15. Loess

Loess is wind-blown clay and fine-sand materials of arid regions which have finally decomposed to plastic clay. It is often found in great beds of considerable thickness. These beds show faint and irregular horizontal stratification. The mass is not very compact and is often permeated to great depths by grass roots or worm casts (connecting holes) lined with lime or different types of clay. Remains of land animals are sometimes found buried in loess. Loess is found in large quantities in eastern Washington near the Idaho line, having been blown from the easily disintegrating basalt of the Columbia basin. Several tons per acre of wind-blown material are still yearly deposited in this region. Such material is without quartz sand and usually gives trouble with shrinking and cracking. It is used to a small extent in the common, red-burning, structural wares. Other loess beds are found in the upper Mississippi and Missouri rivers, in China, and northern Germany.

16. Glacial-lake Clays

This is glacial clay material which has been sorted by stream action and deposited in the temporary lakes which accompany the melting of the ice. Except from the source

of this material, the glacial clays are similar to other young and soft clays used for the commoner dark types of structural wares. The debris from continental glaciers represents a mixture of large land areas and all kinds of rock and clay material over which the ice has traveled. Consequently, the clay deposits in the glacial lakes will be a varied mixture, often containing a large amount of pulverized rock flour having unleached feldspars and basic minerals in but a slightly altered condition. Such materials do not have the tough, bonding plasticity of shales or other clay materials which have been entirely carried by water and have altered to a further degree. On the other hand, their temperature range of vitrification is short, and they easily fuse to smooth red-brown or black glasses with the minimum of vesicular development. Due to the absence of vegetation in these cold waters, the carbon content of the clay material is very low. Because of the temporary character of these lakes and the shifting conditions due to the seasonal changes in temperature and the retreat of the ice mass, a vertical cross-section of a glacial-lake clay bed usually shows a variety of irregular seams from the finest of clay to coarse gravel. Often large boulders are found buried in colloidal clay because some floating iceberg has dropped its load of stones and debris to the ooze in the bottom of the lake.

Since many glacial clays have an undisturbed fusion at comparatively low temperatures, selected beds have long been used as natural, brown-colored glazes for such wares as stoneware and even electrical porcelain. Such materials should possess good adhesive properties for glazing in the plastic and dry condition, should not shrink too much or crack in drying or the early firing periods, and should be able to fuse to a smooth glaze without defects between cones 6 to 10. A number of such beds are found in the neighborhood of Albany, N. Y., and have been used as "slip" clays for many years.[1] Very similar glacial clays

[1] JONES, R. W.: "Albany Slip Clay," *Trans. Am. Ceram. Soc.*, **18**, 242 (1916).

are found near Seattle in the Puget Sound glacial district.[1] In both districts the clays are used for the common structural wares.

17. Weathered Glacial Till

In many places north of parallel 40 in America, the heterogenous collection of glacial debris consisting of unassorted boulders, sand gravel, and clay material has weathered to a workable mass suitable for the common structural wares. This is the case of the surface materials throughout northern Ohio, Indiana, and Illinois. The glacial till of Washington has not weathered sufficiently to produce a plastic mass.

C. CHEMICAL AND MINERALOGICAL COMPOSITION OF CLAY IN THE ORIGINAL CONDITION

Two methods of chemical analysis have been used by ceramists to separate clays into their constituent parts. Both of them give only an approximate idea of the mineralogical composition.

1. "Rational" Analysis

This method has been used to determine the mineral composition of clays directly. Feldspar, quartz, and clay substance are separated by the proper reagents and methods of treatment.

$$\text{Clay} + \left\{\begin{array}{l}\\ \text{hot concentrated } H_2SO_4\\ \text{and boiling } Na_2Co_3\\ \\ \end{array}\right\} = \left\{\begin{array}{ll}\text{soluble} & = \text{clay substance (and mica)}\\ \text{insoluble} & = \text{feldspathic minerals and quartz}\end{array}\right.$$

Al_2O_3 in the insoluble residue $\times$ 3.53 = SiO_2 in feldspar.
SiO_2 in the insoluble residue $-$ (SiO_2 in feldspar) = quartz.
Alkalies + lime + alumina and SiO_2 (feldspar) = feldspar.
Soluble portion = clay substance and mica.

This method of analysis, while subject to serious scientific objections and giving discordant results with the low-grade

[1] Smith, T. O.: "The Shales and Glacial Clays of Puget Sound," *J. Am. Ceram. Soc.*, **8**, 849 (1925).

clays, is nevertheless capable of giving useful data. It is very little used by American ceramists.

Difficulties: (1) The solubility of the different feldspars and kaolins varies in strong acids, and (2) the solubility of the so-called "insoluble" minerals increases rapidly when the particles are the size found in clays.

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Ultimate Chemical Analysis

In contrast to the uncertainties of the "rational" analysis, the ultimate or ordinary chemical analysis can be carried out with great accuracy by the usual methods for the analysis of silicate rocks.[1] The chemical or ultimate composition is expressed in terms of silica, alumina, ferric

[1] Hillebrand, W. F.: "The Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey, Bull.* 422 (1916); Mellor, J. W.: "Quantitative Inorganic Analysis" (1913); Washington, H. S.: "Manual of the Chemical Analysis of Rocks" (1918).

oxide, magnesia, lime, potassium and sodium oxides, water, and other volatile matter, together with the small amounts of titanium dioxide and other rare constituents. Its results stated in terms of the constituent oxides may be readily reduced to mineralogical terms, and a result can be obtained which is more accurate than the short-cut rational-analysis method. Greater accuracy is obtained if a preliminary petrographic analysis is made with the microscope. Mineralogical compositions calculated from chemical analyses are based on a uniform procedure for all clays and rocks, and certain minerals are supposed to be present if their component oxides are found in sufficient amounts. A petrographic examination actually identifies the various minerals, unless they are in the collidal conditions.

3. Calculation of the Mineralogical Composition from the Chemical Analysis[1]

In igneous rocks, the mineralogist deals with solidified solutions, during the solidification and consequent crystallization of which as a mixture of definite minerals, certain laws or so-called "affinity" of the various basic oxides for silica and alumina come into play and determine the actual mineral composition, which changes somewhat with the varying conditions that exist during the solidification. In clays and similar bodies of secondary origin, on the other hand, we are dealing with the remnants of the alteration, decomposition, and disintegration of these minerals, a portion of which are in the colloidal condition.

According to the mineralogical calculation, all clays are assumed to be mixtures of clay substance, $Al_2O_3 2SiO_2 2H_2O$, which may be kaolin or colloidal substances of the kaolinitic type, with quartz and the feldspars. In some clays vary-

[1] Cross, Iddings, Pirsson, and Washington: *J. Geol.*, **10**, 604, 642; Finlay, G. I.: "Introduction to Study of Igneous Rocks," pp. 150, 154, New York (1913); Iddings, J. P.: "Igneous Rocks," **1**, 419, 433, New York (1909); Iddings: "Quantitative Classification of Igneous Rocks," pp. 147, 186, Chicago (1903); Washington, H. S.: "The Calculation of the 'Rational Analysis' of Clays," *J. Am.. Ceram. Soc.*, **1**, 405 (1918).

ing amounts of muscovite, $K_2O3Al_2O_36SiO_22H_2O$, occur. The feldspars are:

Orthoclase / Microcline ..... $K_2OAl_2O_36SiO_2$ (Or) or (Mic)
Albite ..... $Na_2OAl_2O_36SiO_2$ (Ab)
Anorthite ..... $CaOAl_2O_32SiO_2$ (An)

The percentages of the various oxides are reduced to molecular proportions by dividing through by the molecular weights. The molecular proportions of the minerals present are then calculated from the molecular parts of the various oxides.

Method of Distributing the Oxides among the Minerals. 1. The microcline, albite, and anorthite, in the order given, are first determined from the potash, soda, lime, alumina, and silica.

2. The remaining alumina serves as a basis for calculating the kaolin.

3. The silica remaining is quartz.

4. The ferric oxide is the basis for calculating limonite, $Fe_2O_3H_2O$ (Lm).

5. The water remaining from kaolin and limonite is moisture.

6. If carbon dioxide is found, it is assumed to be present as calcite, $CaCO_3$, or with clays high in magnesia, as magnesium carbonate. An equivalent amount of CaO is alloted to the CO_2 for calcite, and the remainder of the lime is calculated to anorthite as above.

7. Magnesia, MgO, is best treated on the assumption that it enters serpentine $3MgO2SiO_22H_2O$ (Sp), the unit of calculation being one-third of the molecular amount of the MgO present. $MgCO_3$ may be present in dolomitic or magnesite districts.

8. Muscovite and hydromica cannot be calculated from the chemical analysis if orthoclase and kaolin are also present. The petrographic examination is useful in this separation. For all practical purposes, however, the potash of any muscovite present may be calculated as orthoclase

and the extra alumina as kaolin, using some of the excess silica for the latter.

9. TiO_2 is usually combined with FeO to form ilmenite, $FeOTiO_2$, and sufficient FeO is taken from Fe_2O_3 (unless the FeO has been separately determined) to produce this combination. Any remaining TiO_2 may be combined with excess CaO, but is usually considered as rutile, TiO_2.

TABLE XI.—METHOD OF CALCULATION—PARTIALLY KAOLINIZED FELDSPAR

	Per cent chemical analysis	Number molecules	Symbol	Per cent mineral composition
SiO_2	75.26	1.2543	Mic	$556 \times 0.0141 = 7.84$
Al_2O_3	15.26	0.1496	Ab	$524 \times 0.1066 = 55.86$
Fe_2O_3	1.04	0.0065	An	$278 \times 0.0066 = 1.84$
CaO	0.37	0.0066	Kl	$258 \times 0.0223 = 5.75$
MgO	1.00	0.0250	Lm	$178 \times 0.0065 = 1.16$
Na_2O	6.61	0.1066	Q	$60 \times 0.4556 = 27.34$
K_2O	1.33	0.0141	Sp	$276 \times 0.0083 = 2.29$
H_2O	1.22	0.0678		

The mineral analysis may be calculated directly without using the molecular ratios. Thus the percentage of orthoclase can be calculated from that of potash by multiplying this by 1.085 for alumina and by 3.832 for the silica and adding the three figures. The amount of alumina so obtained is deducted from the total percentage of alumina in order to get the alumina in the kaolin, etc. The use of tables would eliminate numerous calculations involved.

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4. Value of Chemical Analysis

The purity of the clay can be expressed as the per cent of $Al_2O_3 2SiO_2 2H_2O$ in the total, taking the alumina content as the basis of the clay substance or kaolin calculation. The practical burning test for color is not always sufficient as a test of purity. Clays may burn white and yet be far from the kaolin composition. A clay from Ducks, British Columbia, is a fine-grained, white clay with good plasticity and fires to a white color; yet it contains a large content of magnesia.

Approximate Refractoriness.—A clay high in fluxes, iron oxide, lime, magnesia, alkalies, etc. is less refractory than one low in fluxing material. In general, the refractoriness varies with the alumina-silica ratio but is influenced by the content of fluxes. See the Montgomery method of calculation of the cone fusion point from chemical analysis (Chap. VII, p. 270).[1]

Approximate Fired Color.—The fired color can be estimated by the percentages of iron oxide, lime, alumina, rutile, manganese, and other color-affecting ingredients. Clays with 1 per cent or less of iron oxide usually burn nearly pure white, and those with 1 to 3 per cent iron oxide to some shade of buff. The fired colors of those clays with higher percentages of iron are rather difficult to determine except by actual firing test, as they vary from buff to brown and reds, purples and blacks, depending on the composition, fineness, and state of iron, and the combinations with the

[1] Montgomery, R. J., and C. E. Fulton: *Trans. Am. Ceram. Soc.*, **19,** 303 (1917).

other minerals present in the clay mass (see Chap. VI, p. 159). Likewise the color will vary with the firing treatment.

Chemically Combined Water.—A large quantity of water (above 10 per cent) which cannot be driven off at 110° C. and which on analysis can be separated from the rest of the volatile matter is usually associated with the purer types of clays. Pure kaolin, theoretically contains 13.9 per cent combined water. The allied kaolin minerals like halloysite and allophane, etc. (Chap. II, p. 22) contain even more combined water than kaolin. Ignition loss must not be confused with combined water, because the former may be caused by carbonaceous matter or carbonates.

High Silica.—When the content of silica is high, it is probable that the free quartz sand content will be high, as this is the most common impurity of clays. It is possible, however, to have some of the excess silica present as silicic acid or other forms.

Lime.—A high percentage of lime indicates a clay which has a short vitrification range and early fusion, especially under load in commercial kilns. This is true if the lime is evenly distributed, but if it occurs as limestone pebbles, which are not finely ground during the clay preparation, spalling, and popping of the fired brick will result (Chap. VI, pp. 154 and 160).

Organic Matter.—This material must be removed by oxidation before the surface of the ware is sealed by vitrification or bloating and blackcoring will develop. Those clays having a low temperature of vitrification, and containing carbon must be fired slowly or the oxidation period will extend into the sealing-up or vitrification period. Red-burning clays usually give more trouble than the buff-burning clays, for, in the latter, a greater temperature difference exists between the oxidation period and the vitrification period. If the carbonaceous material is in the form of bituminous or graphitic matter, the difficulty of removal will be greater. The percentage of carbon,

given by the chemical analysis, should be considered in connection with the Fe_2O_3 and the sulphur (also SO_3), as these materials are reduced in the presence of carbon at the higher temperatures. The ease of removal of the carbon is not entirely dependent on the amount present, but likewise varies with the form of carbon, the nature of the accompanying minerals, and the structure of the clay body.

Sulphur.—Combustion gases from sulphur likewise cause bloating and black-coring when not removed by oxidation. Sulphur in the form of sulphate also indicates the presence of the two most common scum- or efflorescence-forming minerals, calcium sulphate and magnesium sulphate. As these do not dissociate until temperatures well in the vitrification range of some low-burning clays, the vitrification period may be shortened by swelling and bloating (see Chap. VI, p. 149). Pyrite or marcasite is also a very common form of sulphur.

The removal of these trouble-forming gases not only depends on the amount and mineral form present but also upon the facility of escape offered by the structure of the body. Non-plastic material, such as sand or artificially added grog, will aid materially with soft, fine-grained clays. With coarsely ground shales where the carbonaceous material is entrapped in the large grains of the shale itself, the best method is to insure a long oxidation period just below the vitrification zone.

Buff-burning clays are, for the most part, more refractory than the red- and brown-burning clays, so that a large carbon and sulphur content is not so objectionable. Their vitrification or sealing-up point is usually above the temperature of gas evolution, and the porosity is sufficient for ready exit.

Summary of the Value of Chemical Analysis.—Chemical analysis provides its most effective usefulness, in the case of the high-grade clays, in estimating the degree of purity of the white-burning, kaolin-like materials and the alumina-silica-flux ratio in the fire clays, but in the case of the red- and brown-burning structural-ware clays, the impurities

furnish the most important data. We can but guess the fired color, strength, shrinkage, porosity, and vitrification range from the analytical data and for these properties, must rely on practical firing tests. If the chemical analysis is complete, however, it gives a good idea of the troublesome materials present, *i.e.*, those which cause early fusion, short vitrification range, scumming, and troublesome gases which delay oxidation. It happens that the usual commercial chemical analysis does not include carbon and sulphur and other troublesome impurities except when combined with the water of chemical combination and called "ignition loss" or "volatile matter." Likewise, a complete chemical analysis of the complicated silicate mixture called "clay" is a difficult analytical procedure, and many hundreds of the analyses are inaccurate.

In studying clays of the whiteware and fire-clay type, a knowledge of the chemical composition is always desirable, but it must be assigned a secondary value because of the influence and modification of the physical properties. Clays of the fire-clay type must primarily have a composition corresponding to refractory clays. But this is not enough. For instance, there are in the United States a large number of clays of practically the same composition as the imported European plastic fire clays, so highly prized for glass-pot, brass, and steel-crucible work, but which fail completely in satisfying the physical, dry, and fired requirements. A cone fusion test costs less in time and money than a chemical analysis. The best way to determine the refractory value of a clay, having given only the chemical analysis, is to translate it to terms of cone fusion.

When physical tests of clay bodies are not satisfactory and changes are desired, the chemical analysis will often locate the trouble and indicate the proper remedy.

5. Soluble Salts

More investigation is needed on the soluble-salt content of clays. While clays represent the end point of silicate rock decomposition, they are not free of soluble materials,

because they contain certain amounts of partially decomposed silicate rocks as sand grains; they are subject to the contamination of ground waters carrying salts in solution and often contain soluble secondary minerals. The colloidal clay particles adsorb certain quantities of these salts to their surfaces, but other salt portions can be removed by washing.

Mellor(2)[1] found that some ball clays released 0.400 per cent soluble salts, while china clays gave only 0.015 per cent soluble matter. Other investigators have found from 0.0 to 1.5 per cent salt content, though it is probable that as high as 5.0 per cent could be obtained from some clays by the proper treatment.

These salts may be divided into two classes: The first includes the very soluble salts of the alkalies or borates. They are of rare occurrence save in the desert or alkali regions. Their distribution is likely to be very irregular; the surface or soil may be heavily loaded while the buried strata may be comparatively free. Such salts have low melting temperatures and act as fluxing materials, particularly on those surfaces which have been exposed during the drying of the clay. They may produce even better colors than those which normally could be produced with the clay and may dissolve the more resistant calcium sulphate scums during firing. Boron or alkali salts are often added to the underglaze clay coatings of terra cotta to provide better adhesion to the body.

The second class of soluble salts is the far more common and troublesome. Calcium sulphate (gypsum) is the worst offender while magnesium sulphate, iron sulphates, and vanadium salts are found in smaller quantities. While one part by weight of gypsum requires 415 parts of water to dissolve it; yet the water used for tempering plastic clay is able to carry enough of the salt to the surface of the ware and deposit a white scum on drying. $CaSO_4$ is not decomposed until about 1200° C. which is above the maximum firing temperature for many red-burning clay wares.

[1] Reference page 54.

The white efflorescence is more apparent against the dark background of red-burning clays than on a buff or white body. During vitrification, however, the silicates of the clay will attack and dissolve the calcium sulphate. Hence, while a soft-fired brick may appear badly scummed, a vitrified product of the same body may be free of "white-wash." Undecomposed sulphate in the interior of a fired-clay body may be brought to the surface by rain or other penetrating waters.

Iron salts are likewise brought to the surface of clay wares. They are not noticed on the red-brown clays but may be found as irregular dark patches on the lighter-colored wares, and may be used to add an attractive polychrome effect to structural brick or tile. Vanadium salts(1)[1] may resist silicate combination to high temperatures and later produce yellow-green efflorescence which may be used to advantage on face brick but which is unsightly on light-colored, slip-coated terra cotta(9). Iron salts may also be responsible for some of the yellow-green scums(8).

In the manufacture of architectural terra cotta another trouble is found from soluble salts. If a coating of calcium sulphate has formed on the surface of the clay body during drying, it is very difficult to obtain perfect contact or adhesion of underglaze coatings which merely vitrify and do not come to a state of complete fusion. Glazes, on the other hand, eat their way through any sulphate coating and produce a strong adhesion to the clay body by solution.

Elimination of Soluble Salts.—The most common method is the addition of barium carbonate, hydroxide, chloride, or fluoride to the clay body before or during tempering. In the case of the carbonate addition, the products of the reaction are the more insoluble calcium carbonate and barium sulphate:

$$CaSO_4 + BaCO_3 = CaCO_3 + BaSO_4.$$

Apparently, calcium hydroxide, calcium chloride, and calcium fluoride do not produce the trouble caused by

[1] Reference page 54.

calcium sulphate, even though the former are more soluble and would be carried to the surface of a drying mass of clay in greater quantities. Calcium hydroxide is rendered insoluble by contact with the carbon dioxide of the atmosphere but is one of the common scums on brick walls with lime mortars or cement mortars which contain free lime. Calcium chloride is strongly hygroscopic. Both the chloride and fluoride are decomposed at comparatively low temperatures during firing. Calcium sulphate can be decomposed at lower temperatures if a reducing atmosphere is maintained in the firing process (see Chap. VI, p. 156).

Amount of Barium Salts Needed.—It has been suggested from various sources that twice the amount of carbonate should be used as that theoretically required to precipitate the sulphates. The active portion of the barium carbonate will vary with the reactivity of the carbonate and the amount adsorbed by the clay particles. Some is lost by the lack of intimate mixing of the salts throughout the clay mass. The amounts commonly used vary from 0.5 to 1.0 per cent of the dry weight of the clay body. While this is in excess of that required, some insurance should be given to take care of the variation of soluble salt content in different shipments and different portions of the clay bank.

Other methods of a more direct nature than the quantitative determination of the soluble-salt content for determining the amount of barium salt needed have been devised: First, in each of a number of 500-cubic centimeter bottles are placed 100 grams of clay and enough water added to fill the bottles three-fourths full. They are shaken thoroughly and allowed to stand until the clay has become finely divided. A 1 per cent solution of barium chloride is then added to each bottle, 1 cubic centimeter to the first, 2 cubic centimeters to the second, etc. The bottles are stored in a warm place for 12 hours with occasional shaking, and after the clay has settled, 100 cubic centimeters of the clear supernatant liquid is drawn off through a filter and a few drops of sulphuric acid added. If turbidity develops, the bottle contained an excess of barium chloride. The

TABLE XII.—SOLUBILITY OF CERTAIN SALTS[1]

Salt	Molecular weight	Solubility in 100 parts of cold water
$CaSO_4$	136	0.179
$CaSO_4 2H_2O$	172	0.241
$CaCO_3$	100	0.0013
$Ca(OH)_2$	74	0.17
$CaCl_2$	111	49.6
$CaCl_2 6H_2O$	219	37.3
CaF_2	78	0.0037
$Ca(NO_3)_2 4H_2O$	236	134
CaS	72	Decomposes
$MgCO_3$	84	0.0106
$4MgCO_3.Mg(OH)_2 5H_2O$	486	0.04
$MgCl_2 6H_2O$	203	167
$Mg(OH)_2$	58	0.0009
$Mg(NO_3)_2 6H_2O$	257	200
$BaCO_3$	197	0.0022
$BaCl_2 2H_2O$	244	36.2
BaF_2	175	0.163
$Ba(OH)_2 8H_2O$	316	5.56
$Ba(NO_3)_2$	261	5.2
BaS	169	Decomposes
$FeCO_3$	116	Insoluble
$FeCl_2.4H_2O$	199	160.1
$Fe(OH)_2$	90	0.00067
$Fe(NO_3)_2 6H_2O$	288	200
$FeCl_3$	162	74.39
$FeCl_3 6H_2O$	270	246
$Fe(OH)_3$	107	Insoluble
$Fe(NO_3)_3 9H_2O$	404	Very soluble

[1] Handbook of Chemistry and Physics, the Chemical Rubber Company.

lowest amount of chloride which develops turbidity is the one to use(4).

The second method is similar to the first, save that barium carbonate is added directly to the clay suspensions in small increasing amounts and barium chloride is added to detect the lack of carbonate. If not enough carbonate has been added to take care of the sulphates, the barium chloride will produce a white precipitate of barium sulphate with the excess of calcium sulphate.

As the chloride and hydrate of barium are readily soluble and an excess would itself produce a coating on the dry

clay body, it has been the practice to add an insufficient amount of chloride or hydrate and make up the balance as carbonate. The latter is very slow in its action. Another method (patented) consists of adding cheap sodium carbonate (soda ash) to precipitate the excess chloride or hydrate. This likewise deflocculates the clay and reduces the water content. An excess is injurious to the hands of the workmen. "Black ash" or the impure soluble sulphide of barium is now on the market and forms a cheaper form of barium salt. It forms barium hydroxide and hydrogen sulphide when wet and hence is rather disagreeable to handle. It is best mixed with the clay in the dry pan.

Determination of the Amount of Soluble Salts.—The quantity and nature of the soluble salts can be determined by solution in pure water, filtration, evaporation, and a quantitative determination of the composition of the filtrate.

Large quantities of water and long periods of time for solution will be needed to dissolve these slightly soluble salts. Boiling water will probably shorten the time of solution but likewise will tend to break down some of the silicates. If the determination is for the purpose of estimating the scumming properties of a piece of fired clay ware, the sample investigated should be that which has been fired to the proper temperature. The colloidal clay will release a large portion of its adsorbed soluble-salt content when heated to low temperatures. This portion is not usually determined by solution at ordinary temperatures. At vitrification temperatures another portion of the soluble salts is taken into insoluble silicate combination by pyrochemical reactions.

The problem of separating the soluble salts in the molecularly dispersed state from the clay particles in the colloidally dispersed condition likewise presents difficulties. The colloidal clay particles will pass through the ordinary filter papers, but will be retained by bisque or alundum filters, which must be operated at low pressures. A much

easier method consists of flocculating the colloids with hydrogen ions from acids or salts, settling the clay, and washing by decantation. The solution of silicates by just sufficient acid to bring the clay to the isoelectric point, should be small. Centrifuging is another method for settling the suspended colloidal matter.

Approximate determinations of the soluble-salt content can be made by the electrical conductivity method, as shown by Bleininger and Kinnison(14).

Reactivity Test for Barium Salts.—The value of barium carbonate for neutralizing soluble salts depends upon its activity when in contact with these salts. Activity test (5):

> Weigh out 2 grams of barium carbonate sample and place in 100 cubic centimeters of a 10 per cent solution of magnesium sulphate. Allow to stand 1 hour at 70° F., stirring at 10-minute intervals with a glass rod. Filter and wash with water until no precipitate shows when tested with barium chloride. Wash precipitate, consisting of barium sulphate and barium carbonate, which has remained unchanged, into a beaker and treat with dilute hydrochloric acid. Collect the barium sulphate now remaining by filtering and washing with warm water until the filtrate is free of barium chloride, as shown by testing with a drop of sulphuric acid. Ignite and weigh. Correct this weight by subtracting the weight of barium carbonate sample which is insoluble in dilute hydrochloric acid. Convert the weight of barium sulphate into terms of barium carbonate ($BaSO_4$: $BaCO_3$ = 233:197), then this weight divided by the weight of the sample of barium carbonate taken, times 100 equals the per cent of barium carbonate which has reacted with the magnesium sulphate.

The test depends on the concentration of the soluble sulphate salt used, the temperature, the kind of soluble sulphate used, and the time. The longer the clay body is aged and the warmer the temperature, the more effective will be the action of the barium carbonate. Grinding a sample of barium carbonate increases its activity, but a finer sample of a different variety is not necessarily the more reactive. Barium carbonate which shows a reactivity in the above test of less than 25 per cent is doubtful material. Commercial witherites at $50 to $60 per ton have shown only 23 per cent reaction, while precipitated

carbonate at $70 to $80 will be from 36 to 38 per cent reactive. The more expensive but readily soluble chloride and hydroxide may prove the cheapest on the basis of the reactivity test.

Methods of Adding Barium Salts.—1. Barium carbonate is commonly added to the clay batch or to one of the clays just before grinding in the dry pan, wet pan, or mixing in the soaking pit.

2. As the per cent of water added to the prepared body in the pugmill is held fairly constant, the carbonate may be added by means of the tempering water. Batches may be weighed and dispersed in water tanks which are provided with constant agitation, and these suspensions are used for tempering as needed. Continuous feeders may supply a constant rate of the powdered barium carbonate to a steady flow of water, based on the average rate of use. Blungers or tube mills can be used for dispersion.

3. The more soluble hydrate or chloride may be fed at a constant rate by a floating siphon(3). Sprinkling the powdered carbonate over the wet clay in a pugmill is a very wasteful, inefficient, and inaccurate method(11).

Scumming or efflorescence may likewise be produced on structural units from sulphur in the fuel used for firing, soluble salts in mortars and other adjoining materials. Green or yellow spots may be fungus growth on porous surfaces.

Individual Properties of Various Soluble Salts.—At this time, only a few of the unsolved portions of this problem can be pointed out. The lime sulphate appears to be the most troublesome salt of efflorescence. This is probably due to its low solubility in water and the ordinary acid cleaning solutions, its ability to cling to rough, fired-clay surfaces and not be removed by rain water or wind, its resistance to decomposition at many of the red-brick firing temperatures, its universal distribution and comparatively large proportion of the soluble-salt content. Calcium hydroxide or lime water, on reaching the surface, is converted to the carbonate which is easily soluble in

dilute hydrochloric acid. The hydroxide of lime is but a temporary form until the carbon dioxide of the atmosphere can change it to the more insoluble carbonate form.

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CHAPTER IV

PHYSICAL CHARACTERISTICS OF CLAY IN THE PLASTIC AND DRY CONDITION

A. PLASTICITY

1. General Definition

Plasticity is that property which enables a material to be deformed continuously and permanently without rupture during the application of a force which exceeds the yield value of the material.[1]

Viscous Liquid versus Plastic Solid.—Theoretically, a viscous liquid will flow with an infinitely small force. Its deformation-pressure curve passes through the zero-zero point. Plastic materials do not flow until the pressure has exceeded a certain yield value.[2] They are then more correctly classified as solids with internal lubrication. Paint, composed of a liquid vehicle and a solid pigment, and plastic clay, composed of water and clay grains, are examples of plastic solids (Fig. 3). The resistance to the viscous flow of liquids has but a single factor—the angle which the curve makes with the pressure axis.[3] The resistance to plastic flow, however, has two contributing factors, (1) the angle the curve makes with the pressure axis and (2) the intercept or yield value f. No single, true unit of plasticity, therefore, can be established. If two plastic substances have the same mobility, the more plastic will have the greater yield value, while if they have the

[1] Bancroft, W. D.: "Applied Colloid Chemistry," p. 183 (1926); "a break is self-healing" in a plastic body.

[2] Bingham, E. C.: "An Investigation of the Laws of Plastic Flow, *U. S. Bur. Standards, Sci. Paper* 278.

Bingham, E. C.: *J. Amer. Ceram. Soc.* **7**, 430 (1924).

[3] "Lime," *Rept. Committee C7, Am. Soc. Testing Materials;* see also, Maxwell: "Theory of Heat."

same yield value, the more plastic will have the higher mobility. See page 59.

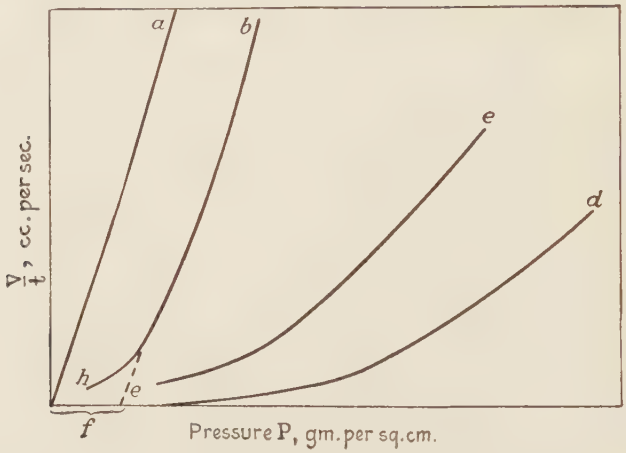


FIG. 3.—Viscous liquids and plastic solids. *a* is the theoretical and experimental curve for true liquids; *bh*, the experimental curve for dilute suspensions, clay slips, paints, etc.; *be*, the theoretical curve for dilute suspensions; *c*, the curve for more concentrated suspensions such as pastes; and *d*, the curve for concentrated suspensions such as very stiff pastes. (*Green, Henry: Am. Soc. Testing Mat.*, **20**, II, 451 (1920).)

Law of Viscous Flow.

$$\phi = K\frac{V}{tP},$$

where

ϕ = fluidity of the liquid.

P = pressure.

$\frac{V}{t}$ = volume of flow per unit time caused by P.

K = a constant.

Law of Plastic Flow.

$$\mu = K\frac{V}{t(P-f)},$$

where

μ = mobility.

f = yield value.

[1] GREEN, H.: Further Development of the Plastometer and Its Practical Application to Research and Routine Problems," *Trans. Am. Soc. Testing Materials*, **20** (II), 451-494 (1920).

For a description of the Bingham-Green plastometer, see Chap. IV, page 109.

The viscous liquids such as glass, asphalt, tar, sealing wax, etc. are moldable with slight forces at the proper

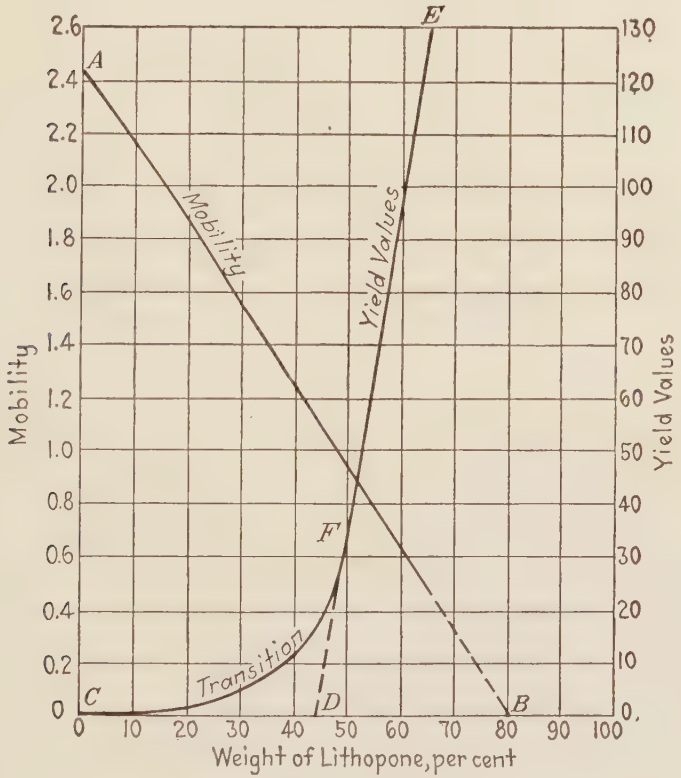


FIG. 4.—Mobility and yield values found by the addition of lithopone to linseed oil. The *C-F* portion of the yield value curve is the transition period between a viscous liquid and a plastic solid and may be called the *pseudo-plastic* condition. (*Bingham, E. C.: J. Am. Ceram. Soc.*, **7**, 376 (1924).)

temperature, harden or become extremely viscous at lower temperatures, and yet will deform under their own weights if given sufficient time. Bingham, however, by mixing sand with the viscous tar was able to produce a plastic solid which resisted deformation for long periods of time when suspended at the ends. According to the general

definition, most metals are plastic solids which require a very high initial pressure to start flow or deformation.

2. The Plasticity of Clays

The following concepts are associated with the plasticity of clay:

1. Clay (hydrous aluminum silicates of variable composition) as the solid.
2. Water as the liquid coating for the clay grains.
3. Moldability with small pressures such as with the hands.
4. On drying or elimination of the water, a coherent brittle mass is produced, stronger than the plastic clay.
5. On the uniform addition of water, the original plastic condition must be restored if the drying temperature has not been carried above 75° C.
6. On heating to incandescent temperatures, the maximum strength is produced by fusion and chemical interaction of the various ingredients. (Nos. 4, 5, and 6 are related only indirectly to the actual plasticity.)

Yield Value for Clays.—Bleininger[1] found that from 33 to 84 pounds per square inch pressure was required to start initial flow of various clays in the plastic working condition through an orifice 0.25 inch in diameter. The pressure varied inversely with the water content, and the plotted relationship gave a hyperbolic curve. Atterberg (Chap. IV, p. 112) also used this conception of flow for his lower plasticity limit. J. W. Mellor[2] has shown that the water content necessary to produce the maximum plasticity as shown by the state of stickiness decreases with the pressure applied. By increasing the pressure from 1.0 to 200 kilograms per square centimeter, the water content for stickiness was reduced from 26.4 to 5.6 per cent in an

[1] Bleininger, A. V., and D. V. Ross: "The Flow of Clays under Pressure", *Trans. Am. Ceram. Soc.*, **16,** 396 (1914).

[2] Mellor, J. W.: "On the Plasticity of Clays," *Trans. Ceram. Soc. (England)*, **21,** 95 (1921–1922).

earthenware body. Hall[1] found yield values of 50 grams per square centimeter for an English china clay and 395 grams for an English ball clay (see Fig. 5).

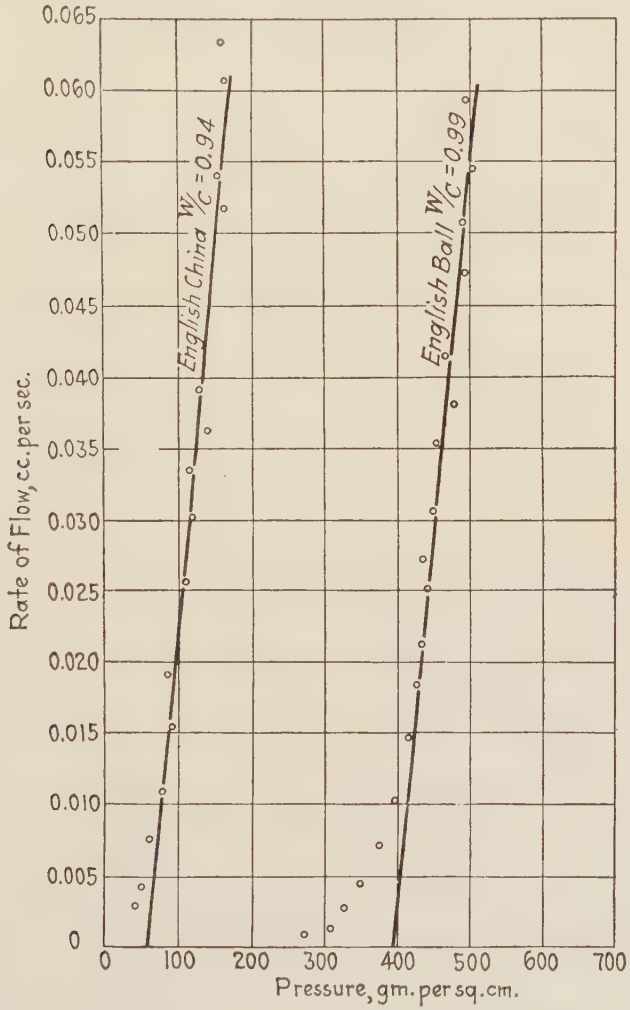


FIG. 5.—The yield value of two clays which have been brought to the same mobility by varying the water to clay ratios. The English ball clay with the yield value of 395 grams per square centimeter is more plastic than the English china clay with a yield value of only 50 grams. (*Hall, F. P.: J. Am. Ceram. Soc.*, **5**, 352 (1922).)

[1] HALL, F. P.: "The Plasticity of Clays," *J. Am. Ceram. Soc.*, **5**, 352 (1922).

The Cause of the Plasticity of Clays.—The cause of plasticity has been the source of considerable research and the development of a number of theories. The latter can be divided into two classes—first, those theories which attempt to explain the fundamental source of plastic and dry strength, and second, those theories dealing with phenomena which tend to influence or vary the plastic strength developed from one of the fundamental sources.

1. Fundamental theories:
   a. Molecular attraction
   b. Surface tension
2. Secondary influences:
   a. Colloidal condition
   b. Organic or bacterial action
   c. Shape, size, and distribution of sizes of non-plastic grains, and the comparative amount of non-plastic material present

3. Colloidal Nature of Clays and Relation To Plasticity

Colloidal Chemistry. Introduction.—In connection with the plasticity of clays, so much confusion has arisen in the discussion of the colloidal condition that a few of the fundamental ideas from recent publications on colloidal chemistry will be repeated.[1] The word "colloid" comes from the Greek word for "glue."

Bancroft[2] adopts a very flexible definition and states that "a phase is called colloidal when it is sufficiently finely divided. Colloidal chemistry is the chemistry of bubbles, drops, grains, filaments, and films, because in each of these cases at least one dimension of the phase is very small." With this conception in mind, we can combine the so-called colloidal theories of certain ceramists with the molecular-attraction and surface-tension theories

[1] Ostwald, W.: "A Handbook of Colloid Chemistry;" Bancroft, W. D.: "Applied Colloid Chemistry—General Theory" (1921); Alexander, Jerome: "Colloid Chemistry," D. Van Nostrand Company (1919); Hatschek, E.: "Physics and Chemistry of Colloids."

[2] *Loc. cit.*

of others, because in plastic clay we are dealing with colloidal matter, combined with minute grains and surrounded by water films.

Extracts from Ostwald's "Handbook of Colloid Chemistry" give the following:

> All substances can appear as colloids under appropriate conditions. Colloidal chemistry presents itself not as a study of colloid substances but as the study of the *colloid state*. The same chemical compound can appear as a colloid or as a non-colloid. Colloid properties are in no way connected with substances of definite chemical composition. We can speak of colloids only as we speak of crystals, amorphous substances, soluble and insoluble substances, or better still, of gaseous, liquid, and solid substances. Solid and liquid and even gaseous bodies may appear in the colloid state.

A colloidal substance is not necessarily amorphous. Nearly all colloid solutions belong to the class of chemically heterogeneous liquids in contrast to the chemically homogeneous liquid, which (1) can be evaporated or frozen without changing its composition at any time during manipulation and (2) has only one boiling temperature and one freezing temperature. Chemically heterogeneous liquids can be separated by changes in temperature and pressure into at least two components of different chemical composition. These heterogeneous liquids may appear in any one of three states:

1. The ordinary "true" (molecular dispersion) solution of one or more substances.
2. Colloidal solution.
3. A coarse mechanical suspension of one or more substances.

The colloidal solution lies between the true solution and the coarse suspension. In the true sense of the word a "colloidal solution" is not a solution as it contains more than one phase. The "dissolved substance" is not present in the form of simple molecules but rather as comparatively large aggregations of molecules, but which are still very small when compared with ordinary dimensional units.

Difference between True Solutions and Colloidal Solutions.—The colloidal solution exhibits:

1. A very low rate of diffusion.
2. The Brownian movement.
3. Small osmotic pressures.
4. The phenomena of electrophoresis and electrosmosis.
5. The phenomena connected with electrolytic and chemical coagulation.
6. Adsorption.

Absolutely clear liquids are formed as a rule by substances in molecular or true solution. If the liquid is turbid and is not chemically homogeneous or a coarse suspension, it is probably a colloid solution. Slight turbidity may be detected by placing a thick layer of the liquid against a black background or by allowing a ray of light to pass through it when in a darkened room. The illumination of the particles from a single side makes them visible. By the use of ultra methods of filtration through ultra filters of collodion and gelatine jellies of appropriate permeability, not only may colloids be separated from crystalloids (substances in true solution) but different-sized colloid particles may be separated from each other. Animal, plant, and special artificial membranes will hold back the colloids and allow the true solutions to pass.

The Properties of Mechanical Suspensions.—Mechanical suspensions of substances but slightly soluble in the liquid, such as quartz or kaolin particles in water, are turbid in transmitted light. Their individual particles can be recognized under the microscope, though sometimes only with high magnifications and special optical devices.

Filtration is another method by which a suspension can be recognized. Ordinary filter paper retains particles having a diameter greater than about 5 microns or 0.005 millimeter, but allows colloids to pass through. A hardened filter retains particles about 2 microns in diameter. Fired clay cylinders will even hold back particles about 0.4 to 0.2 micron in diameter. The size of the particles in suspension can then be roughly measured by the employment of

such filters. By settling naturally or by centrifuging, a separation of the suspended particles and the liquid can be easily effected. The original system, however, can be restored again by mechanical agitation or shaking. When the suspended particles are in a very finely divided condition, indefinite or negative results are obtained by the above procedures. High-speed centrifuging is now used for the separation of colloids of various sizes.

R. Zsigmondy has developed a classification on the degree of subdivision. Particles visible under the microscope are termed "microns," while those which can be seen only by the application of the ultramicroscopic methods are called "submicrons or ultramicrons." The disperse phase of colloid solutions would, therefore, be made up of submicrons or ultramicrons. The value of 0.1 micron represents about the field of microscopic visibility. The field of colloid chemistry begins with particles of this size and extends down to particles about 1.0 millimicron (0.001 micron) in size. Some of the estimated diameters of the molecules of the true solutions are as follows:

		Millimicron
Smallest:	Hydrogen gas	0.067–0.159
	Water vapor	0.113
	Carbon dioxide	0.285
	Sodium chloride	0.26
	Sugar	0.70

Brownian Movement.[1]—The Brownian movement is a microscopically observed agitation of suspended particles and is caused by the bombardment of them by the molecules of the liquid medium. The existence of colloidal solutions is dependent on the Brownian movements counteracting the force of gravity.[2] By increasing the force of gravity, as in the centrifuge, a colloidal solution may become less stable and precipitate. High-speed centrifuging is now used for the separation of colloids of various sizes. Such is the case with milk and cream. The Brownian movements

[1] *Phil. Mag.*, **4**, 161 (1828); **6**, 161 (1829).

[2] BANCROFT, W. D.: "Applied Colloid Chemistry," p. 137 (1921).

cause diffusion by making the colloid particles distribute themselves more uniformly throughout the liquid. When the very finely divided particles coalesce or agglomerate, the Brownian movements diminish or cease, and settling is accelerated.

Types of Precipitates.—When the colloidal particles are in suspension as the result of the Brownian movements and have not been coagulated, the solution is called a "sol." One may use the words "hydrosol," "alcosol," etc., to show that the dispersing liquid is water, alcohol, etc. When the colloidal particles agglomerate and precipitate, the precipitate is called a "gel," or a "hydrogel" in case the dispersing liquid is water. The word "gel" is also used to include a jelly, which differs from a gelatinous precipitate in that there is no supernatant liquid when first formed. Gel is then the general term for a solid or semisolid colloid. Gel is the inclusive term, gelatinous precipitates and jellies being two forms of gels. The change from a gel to a sol is usually called "deflocculation," "dispersion," "solation," or "peptization." The reverse change from sol to gel was called "pectization" by Graham, but is now usually expressed as "coagulation." A stable colloidal solution (sol) will consist of very fine particles kept from agglomerating by a protecting film of some sort, electrification being equivalent to a film. Small particles may be obtained either by condensation from vapor or solution (usually by precipitation) or by mechanical disintegration of larger masses.

The clay colloid is a reversible one. In neutral or alkaline solutions, the clay particles, between 0.1 micron and 1.0 millimicron in size, move independently of each other, cannot be seen under the ordinary microscope, and are in the sol or dispersed state. In acidic solutions, the sol flocculates, precipitates, or coagulates. The massing or grouping of the particles into clusters can be seen under the microscope. The change of state is easily effected with the proper amount of alkali or acid. Likewise, if the mechanical and adsorbed waters are removed by drying, the clay may be brought back to the colloidal solution again by the

simple addition of water. If the temperature is raised beyond the dehydration temperature of the chemically combined water, however, an irreversible set gel condition develops, and the mass loses its ability to become plastic again save by processes similar to those by which the original parent igneous rock was transformed into plastic clay.

Electric Charge and Migration.—The particles of practically all colloidal solutions possess an electric charge, and under the influence of an electric current (difference of potential) move toward the electrode having the opposite charge. Ralston[1] suggests the following definitions:

"*Electrolysis*" is a term universally accepted as meaning the act or process of chemical decomposition by means of the electric current.

"*Electrosmosis*" is proposed to supplant such terms as electric osmose, electrical endosmose, electric endosmosis, electro-osmosis, etc. All these terms mean the passage of liquids through diaphragms (osmosis) due to the application of electrical forces.

"*Electrophoresis*" means the travel, transport, or wandering of a particle of solid, liquid, or gaseous matter suspended in a mobile medium, liquid or gaseous, when a unidirectional electric stress is applied.

"*Cathodophoresis*" is proposed to mean migration of suspended particles toward the cathodes when under the influence of a unidirectional current.

"*Anodophoresis*" is proposed to mean migration to the anode.

When suspended in water, particles of clay, shellac, quartz, cotton, starch, graphite, sulphur, gum arabic, silicic acid, etc. travel to the positive electrode. When free ions are adsorbed by particles suspended in a liquid, the particles will behave to some extent like an ion and will tend to move under electrical stress in the normal direction of the adsorbed ion. If the particles are suspended in gases, very high voltages must be employed to ionize the gaseous molecules and bring about precipitation, as is shown in the Cotrell process. No electrophoresis is

[1] Ralston, O. C.: "Electrosmosis and Electrophoresis, Two Definitions," *Chem. Met. Eng.*, **27** (16), 778 (1922).

noted in liquids like chloroform, ether, petroleum, oil of turpentine, etc. (The dielectric constants of these liquids are low in comparison with water.) Hydroxyl ions raise the migration velocity of a negatively charged clay to the positive pole, while acids decrease it to zero with increasing concentration and finally change its sign.[1] Soluble salts in clays complicate the process. The presence of salt solutions may produce changes of the charges on the particles or complicated hydrolytic reactions, for we are dealing with some slightly soluble weak acids, whose salts are hydrolyzed and but slightly soluble with the exception of those of the alkalies and ammonia.

Cause of the Charge on the Particles.—1. A practically discarded theory states that the charge is due to the frictional contact between the particles and the medium.

2. Ionization of some foreign substance present in the colloid at the moment of formation.

3. Actual ionization of the colloid itself.

4. Preferential adsorption at the surface of the colloid of ions present in the dispersion medium.

Hydrogen-ion Concentrations of Clays.—The hydrogen-ion concentration is the degree of acidity. It is therefore different from the amount of acid or acid concentration. 0.01 normal HCl and 0.01 normal acetic acid may contain equivalent amounts of acid determined by titration with standard alkalies, but the hydrogen-ion concentration in the case of the hydrochloric acid will be 25 times greater than that of the acetic acid. The following are the various

[1] FREUNDLICH: "Kapillarchemie," p. 239.

NOTE.—F. P. HALL, quoting MATTSON, S. E.: "Effect of Hydrogen-ion Concentration upon Clay Suspensions," *J. Am. Ceram. Soc.*, **6** (9), 999 (1923), agrees that the clay particle becomes positively charged with increasing acidity. However, Richard Bradfield ("The Chemical Nature of a Colloidal Clay," *Univ. Missouri Agr. Exp. Sta., Research Bull.* 60, 36 (1923) found that an excess of acid did not cause a reversal in the sign of the charge of the clay particles with which he was working. Experiments in the ceramic laboratory, University of Washington, Seattle, showed that some kaolins studied did not travel to the negative pole with an excess of hydrogen ions.

methods used to indicate the same concentration of hydrogen ions:

$$\frac{1}{100{,}000}\text{N}, \quad (1)$$

$$0.00001\text{N}, \quad (2)$$

$$1 \times 10^{-5}\text{N} \quad (3)$$

and pH 5.0 (4)

The fourth is called the Sorensen or the pH value. It is the logarithm of the reciprocal of the hydrogen-ion concentration. The dissociation constant of water at 25° C. is about 10^{-14}, and, since in pure water $H^+ = OH^-$, the pH value of pure water is 7.0. In comparison with water, a solution with a pH value less than 7 is acid, and one greater than 7 is alkaline. The method in common use for measuring the pH value of solutions is the electrical one using the hydrogen electrode.[1]

The pH values of the water extract of several clays in the concentration $\frac{W}{c} = \frac{4}{1}$ was determined by Hall[2] at the United States Bureau of Standards:

TABLE XIII

Clay	pH
English china clay	5.20
Bentonite	9.72[a]
North Carolina kaolin	4.75
Florida kaolin	5.90
Georgia kaolin	4.15
H. and Walker fire clay	5.00
Stoneware grog	6.10
English ball clay	4.65
J. P. Tennessee ball No. 9	5.50
Kentucky ball clay No. 4	5.20

[a] Water-clay ratio is 70: 1.

The pH values varied from 3.0 to 8.5. No generalization was possible in comparing the pH values with different

[1] CLARK, W. M.: "The Determination of Hydrogen Ions," Williams and Wilkins Company, Baltimore (1922); *Catalogue* 75, *Bulls.* 765, 767, Leeds and Northrup Company, Philadelphia, Pa.

[2] HALL, F. P.: "Effect of Hydrogen-ion Concentration upon Clay Suspensions," *J. Am. Ceram. Soc.*, **6** (9), 991 (1923).

types of clay. The hydrogen-ion content varied with the adsorbed-salt contents. After a series of washing tests, Hall found that those clays which, with the first addition of water, gave an acid extract decreased in acidity with successive washings, and those clays which at first gave the alkaline extract usually decreased in alkalinity with further washing. Hall[1] was not able to determine whether ageing increased the hydrogen-ion content or not.

Commercial Applications of Electrophoresis in Clay Purification.—Following the work of German investigators Bleininger[1] built an electrical anodophoresis machine at the United States Bureau of Standards and separated such materials as flint, feldspar (poor separation), kaolin, and impure fire clay, respectively, from their water suspensions and to a minor extent from the positively charged, iron-bearing mineral impurities. His apparatus consisted of a copper tank in which a revolving drum was used as the positive electrode. A thin layer of clay drawn from the suspension in the tank was scraped off the drum as it revolved. His general conclusions in regard to this apparatus were that,

> with the general run of clays the suspended clay will be deposited by the electric current just as it is, and if it has not been subjected to a (chemical) sedimentation process . . . the quality of the product will not be superior to that of ordinary washed clay. If the electrical continuous separation can replace the filter press economically, its use would be justified.

A commercial anodophoresis kaolin purification factory is operating at the present time in Germany. The conclusions of an English investigator, Hind,[2] are very similar to those of Bleininger's. The anodophoresis machine acts as a filter press and the purification of the kaolin is dependent on chemical sedimentation processes.

[1] Bleininger, A. V.: "Use of Sodium Salts in the Purification of Clays and in the Casting Process," *U. S. Bur. Standards, Tech. Paper* 51, 16 (1915).

[2] Hind, S. R.: "A Visit to the Osmosis Plant at Carlsbad," *Trans. Ceram. Soc.* (*England*), **24,** 73–85 (1924–1925).

Deflocculation, Dispersion, or Peptization.—Clay suspensions in pure water usually give no reaction when tested with the common indicators, though they may be either acidic or alkaline, depending on the kind and strength of contaminating salts and their selective adsorption of salts. When the proper amount of alkali is added, however, the viscosity of the liquid will decrease and the particles will remain in suspension[1] for a greater length of time (Fig. 6). Also a cleaner separation can be made between the coarse, non-plastic material and the finely divided, clay-like particles. The clay is said to be in the deflocculated condition (analogous to the sol form of colloids). When filtered through ordinary filter paper or commercial filtering canvas, the filtrate will show turbidity. Such a colloidal suspension, after the coarser particles have been allowed to settle, will give rise to the phenomenon of the Tyndall cone when a beam of light is passed through it. The addition of alkali to a clay suspension increases the negative charge on the particles until a certain point is reached where further additions decreases the charge. The point of maximum charge occurs in the region of maximum deflocculation.[2] For every clay-water-electrolyte mixture there is a pH value at which the rate of settling of the clay is a minimum. This point of maximum deflocculation is not definite, because undoubtedly we are dealing with a mixture of colloids and not a single colloid. Hall[3] found that the point of maximum deflocculation varied for different clays between pH 11 and 12.0.

Stabilization of Deflocculated Colloidal Solutions.—The stabilization of a colloidal solution may be due to (1) an adsorbed liquid; (2) an adsorbed undissociated substance in true or colloidal solution; or (3) an adsorbed ion. As long as the particles are all charged alike they will not

[1] With high concentrations, the larger particles may sweep the truly colloidal particles down with them as they settle.

[2] Hall, F. P.: "Effect of Hydrogen-ion Concentration upon Clay Suspensions," *J. Am. Ceram. Soc.*, **6** (9), 999 (1923).

[3] *Loc. cit.*

coalesce unless the concentration is too high.[1] If the charge is neutralized or counterbalanced in any way, the particles will gather in groups and precipitate. Deflocculated clay suspensions are hence very sensitive to most electrolytes of the opposite charge to that which the clay carries. The amount of opposing electrolyte necessary to

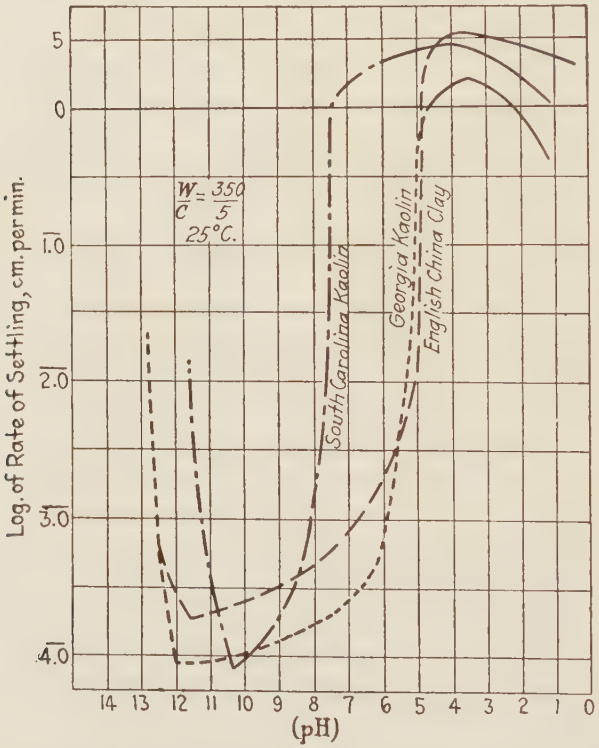


FIG. 6.—The relation between the rate of settling of three kaolins and the pH value of the suspending medium. The full lines indicate the average rate of settling of the flocculated clay and the broken lines indicate the rate of settling of the finest particles over the deflocculated range. (*Hall, F. P.: J. Am. Ceram. Soc.*, **6**, 994 (1923).)

bring the solution to the isoelectric point varies with the nature of the dispersed phase. In other words, the amount of acid needed to coagulate the clay suspension which has been deflocculated by an alkali is not necessarily equal to that needed to neutralize the alkali.

[1] BANCROFT, W. D.: "Applied Colloid Chemistry," 285 (1926).

Time Effect.—The viscosity of most clay slips, casting bodies, and glazes changes with time. Casting bodies after deflocculation tend to develop a coagulated condition and increase in viscosity on standing.[1] The slips which contain just enough alkali to bring them to the state of maximum deflocculation are likely to show this change more than those which contain an excess. This may be due to the continued reactions between the alkalies and the soluble sulphates, to a continued adsorption of the electrolytes, or to a continued disintegration of the clay particles.

Protective Colloids.—Colloids like gelatine, gum arabic, dextrine tannins, etc., which are dispersed easily by the action of water alone, will deflocculate many precipitates and are often called protective colloids because they tend to prevent the agglomeration and subsequent settling of finely divided precipitates in the presence of acids or flocculating salts. When gum arabic is used in glaze work to provide a better adhesion to the clay body, the glaze suspension will respond but feebly to the action of acids. A protective colloid may not be able to deflocculate a clay slip itself and yet may prevent or retard the flocculation and precipitation by another material. When the clay particle adsorbs a protective colloid, the surface or the active portion is so coated that the nature of the particle changes toward that of the protective colloid. Glues, gums, and organic byproducts from slaughter houses act as retarders in the setting of calcined gypsum.

Concentration Effect of the Electrolyte.—The first addition of alkali brings about a decided minimum in the viscosity-concentration curve of clay suspension, but this may be followed by a succession of maxima and minima until finally the phases merge in a definite direction.[2]

[1] Bleininger, A. V.: "Use of Sodium Salts in the Purification of Clays and in the Casting Process," *U. S. Bur. Standards, Tech. Paper* 51, 37 (1915).

[2] Bleininger, A. V.: "Ceramic Processes Associated with Colloid Phenomena," *J. Ind. Eng. Chem.*, **12** (5), 436–438 (1920); Kirkpatrick, F. A.: "An Attempt to Fit Enamels to Plastic Clay Bodies," *Trans. Am. Ceram. Soc.*, **18,** 139 (1916); Bole, G. W.: "Mechanism of Plasticity from a Colloid Standpoint," *J. Am. Ceram. Soc.*, **5** (8), 472 (1922).

The same is true when acids are added to the clay suspension, save that a maximum viscosity is first obtained in the curve.

Flocculation, Coagulation.—The addition of acids and many salts to an alkaline clay slip will first neutralize the alkali and bring the slip back to the neutral condition (agglomeration) where it can be filter pressed or dewatered without producing a milky filtrate (see Fig. 7). Such additions increase the viscosity, the degree of plasticity,

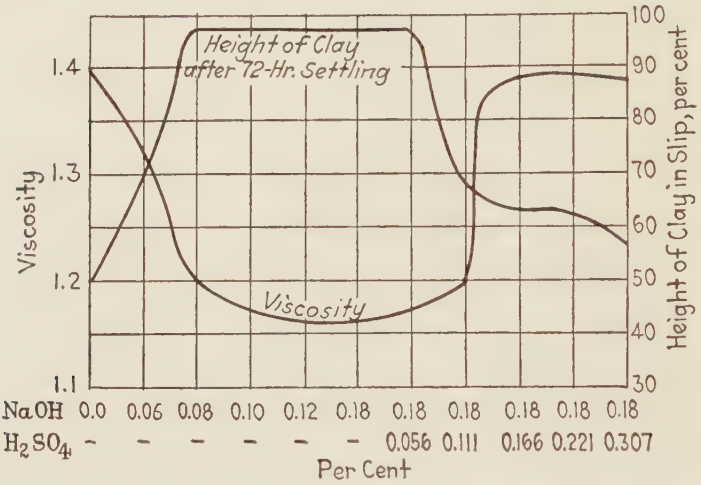


Fig. 7.—Settling and viscosity data of Georgia kaolin slip with NaOH and H_2SO_4. (*Schurecht, H. G.: Trans. Amer. Ceram. Soc.*, **19**, 460 (1917).)

and the water content required for standard consistency with most clays. Under the microscope, the clay particles of visible size play around freely in the neutral or alkaline condition, but as soon as acidified, the system becomes tense, and the particles collect in loose agglomerations. These groups act as units and hold water in the voids of the groups. It has been suggested that in this condition, the clay particle itself has swelled like a sponge and absorbed a large quantity of water; but such a theory is not necessary for our conception of plasticity. In either case, the size of the unit has increased, and, according to Stoke's law, the rate of settling will increase as the square of the radius, although the specific gravity will change toward that of water.

Stoke's law,

$$v = \frac{2r^2g(d-d_1)}{9k}$$

where

v = the velocity of settling in centimeter per second,
r = the radius in centimeters of the particles,
d = the density of the particle,
d_1 = the density of the liquid,
g = the gravity constant (980),
k = the viscosity, about 0.01 for water.

Pickering[1] believes that the size of the particles increases upon flocculation because the Brownian movements have ceased. This increase in size cannot be detected under the microscope and hence is believed by Pickering to be due to a combination of the particle with the transparent fluid which acts as a buffer against molecular bombardment. The increased volume shown on subsidence is from 100 to 200 per cent and so represents several hundred molecules of water in combination with the clay (Fig. 8).

For every clay-water-electrolyte mixture a certain pH value, called the "isoelectric point" can be found at which the settling rate of the clay is a maximum. The charge on the particles is zero at this point. Hall[2] found that the isoelectric points for several clays were not the same but varied between pH 2.7 and 4.0. Neither the isoelectric point nor the point of maximum deflocculation is very well defined, owing to the composite character of the colloidal portion of the clay.

Glaze suspensions containing feldspar, clays, calcium carbonate, zinc oxide, barium carbonate, lead oxides, etc. are commonly brought to the flocculated condition with hydrochloric acid to increase the viscosity of the fluid for better application to the clay bodies and to prevent differential separation of the plastic and non-plastic portions when standing. While the rate of settling is increased,

[1] Pickering, S. U.: *Proc. Roy. Soc.*, **94**, 315 (1918); *Trans. Ceram. Soc. (England)*, **17**, 116 (1916–1917).

[2] *Loc. cit.*

the mass settles together and can be easily floated again by stirring. The viscosity usually drops in a short time, however. This may be due to the continued neutralization effects of various alkalies in the complicated mixtures or in some cases, due to the emergence of the air entrapped during the grinding process. Bancroft states that all precipitates tend to become coarser and more firmly agglomerated with standing.

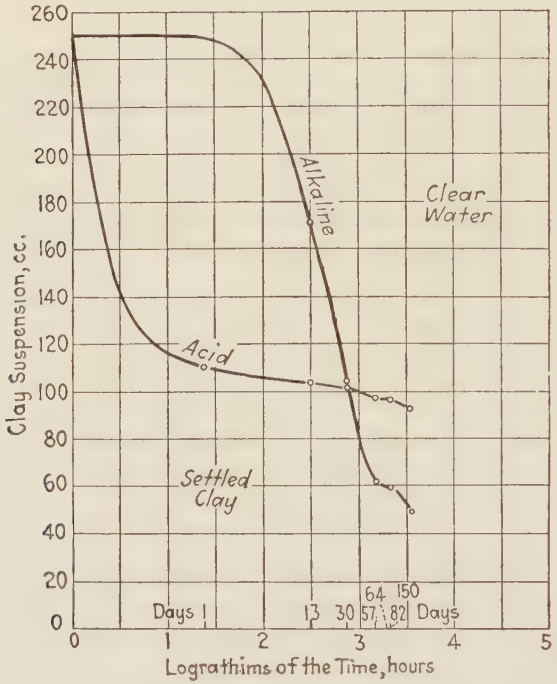


FIG. 8.—Rate of settling and volumes of settled clay suspension of the same Washington kaolin when dispersed with alkali and when coagulated with hydrochloric acid.

COMMERCIAL USES OF FLOCCULATION AND DEFLOCCULATION OF CLAYS

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3. Back, Robert: "Effect of Some Electrolytes on Clays," *Trans. Am. Ceram. Soc.*, **16,** 515 (1914).
4. Bleininger, A. V., and Hornung: "Notes on Casting," *Trans. Am. Ceram. Soc.*, **17,** 330 (1915).
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15. Bleininger, A. V.: "The Use of Sodium Salts in the Purification of Clays and in the Casting Process," *U. S. Bur. Standards, Tech. Paper* 51 (1915).
16. Sproat, Ira A.: "Refining and Utilization of Georgia Kaolins," *U. S. Bur. Mines, Bull.* 128.

Refining of Kaolins.—The "chemical" process for the purification of kaolins can be divided into eight steps:[1]

1. Storage and disintegration to provide sufficient raw material of constant size of lump and water content for uniform feeding.

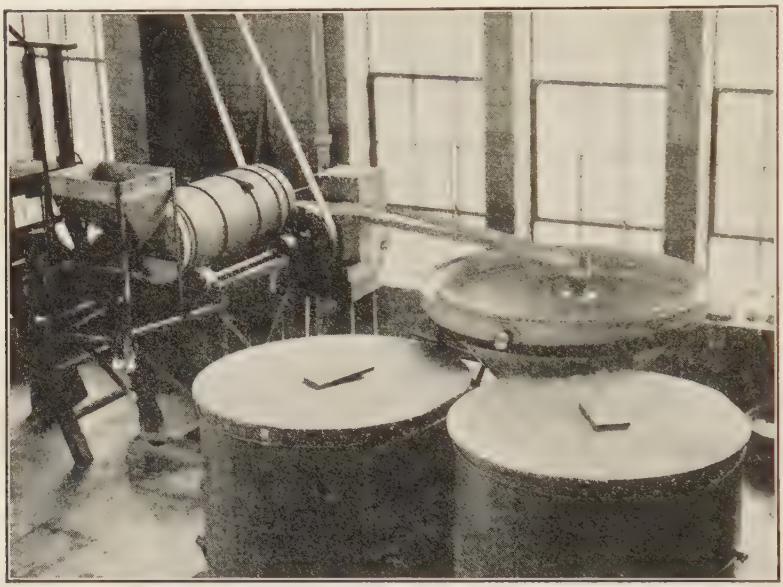


FIG. 9.—Simple type of laboratory kaolin-washing apparatus. Left-hand side of photograph shows hopper for crushed clay with screw and water feed at bottom. Clay and water are fed into rotating blunger which overflows into sand box and on into cone where the finest sand and mica are deposited as the clay slip flows from the center to the circumference. The overflow from the cone is caught in either of the two settling tanks in the foreground and coagulated with acid. (*Clark, Roland: University of Washington, Seattle.*)

2. Thorough blunging in water and partial dispersion of the clay particles.

3. Deflocculation and complete dispersion by the addition of the proper amount of alkali to the clay slip in the blunging apparatus.

4. Flotation: first in tanks to catch the coarse sand which settles rapidly, and then in troughs, cyclone separa-

[1] SPROAT, I. A.: "Kaolin Refining," *Trans. Am. Ceram. Soc.*, **18**, 767 (1916).

tors, Dorr bowl classifiers, or Callow cones to settle the fine sand and mica in slow-moving currents[1] (Fig. 9).

5. Coagulation with just enough acid to bring the system to the isoelectric point.

6. Screening to remove the floating impurities.

7. Concentration by settling and decantation.

8. Final dewatering to dryness in filter presses, atmospheric drum dryers, spray dryers, or rotary dryers.

The Function of Alkalies in the Casting Process.—Many ceramic articles from small pottery wares to large glass pots are made by pouring clay slip into plaster or calcined gypsum molds. The porous "plaster of paris" absorbs the water, and a layer of clay adheres to the inner walls. When a sufficient thickness is obtained, the excess slip is poured out, and the adhering clay skin is partially dried and removed after shrinking from the walls of the mold. Additions of alkali (about 0.3 per cent Na_2CO_3 and Na_2SiO_3) decrease the amount of water required to hold the clay in a suspended state and yet provide sufficient fluidity to permit pouring. In fact, in many cases, the water content is no greater than that of the same mixture in the plastic state, without alkali. Or, in other words, if the dry alkali is added and mixed with the plastic mass of clay, it will become fluid enough to pour. Subsequent drying shrinkage and the accompanying cracking are thus reduced. The point of minimum viscosity is determined by the use of viscosimeters.

Dried Pottery Scrap.—When in pottery work the dry scrap clay is reblunged with fresh clay, the proportion of the old material must be controlled or a loss of plasticity and strength of the mixture is noticed and trouble with cracking is often experienced. This is apparently due to a partial setting of the colloidal matter caused by the heat of the dryers (see p. 137). The original plasticity may be restored by the addition of such salts or acids as hydrochloric, magnesium sulphate, calcium sulphate, and vinegar

[1] Clark, Roland: "Refining of Pacific Northwest Kaolins," *J. Am. Ceram. Soc.* (1927).

in amounts varying from 0.05 to 0.10 per cent. 0.07 per cent $MgSO_4$ has been used on a commercial scale for this purpose.[1]

Body and Glaze Suspensions.—A peculiar condition exists in the aqueous suspensions of non-plastic particles in bodies and glazes. Non-plastic particles of flint and feldspar will settle immediately and form a dense mass in the bottom of the container. Finely divided clay will remain suspended for long periods. The addition of sufficient clay will float the feldspar and flint for some time, and, when the mass does settle, it will come down in a more uniform mass and the tendency to cake in the bottom will be lessened. The coarser particles interfere with the finer ones and tend to carry them down, while the finer sizes, suspended by Brownian agitation, tend to float the coarser particles. Such a mass, after settling, can be easily stirred and mixed with the clear water above. Acids will increase the viscosity of the glazes and increase the carrying power, but the mass as a whole will settle more quickly. Alkalies will lower the viscosity, allow more of a separation and settling of the coarser grains but a longer suspension of the finer clay particles. In a like manner, if the suspension is too dilute, the viscosity will be low, permitting differential settling of the grains of various sizes.

When hydrochloric acid is added to a terra cotta glaze, it is readily neutralized by the calcium and barium carbonates and zinc oxide. Nevertheless, the viscosity increases as the hydrogen-ion content is raised.[2] $ZnCl_2$, $SnCl_4$, and $AlCl_3$ gave a far greater increase in viscosity than $CaCl_2$. The action of the common electrolytes is far greater with the glazes where the clay content is comparatively low than it is with clay slips and whiteware bodies containing larger clay contents.

[1] Minnemann, J.: "Note on the Restoration of Plasticity to Pottery Scrap Clay," *Trans. Am. Ceram. Soc.*, **16**, 97 (1914).

[2] Kirkpatrick, F. A., *et al.*: "An Attempt to Fit Enamels to Plastic Clay Bodies," *Trans. Am. Ceram. Soc.*, **18**, 139 (1916).

The Colloid Content of Clays.[1]—Clays are mixtures of colloidal hydrated aluminum silicates with granular matter consisting of quartz, feldspar, mica, and other minerals which vary in size of grain from coarse sand to very fine particles approaching colloidal dimensions. The colloidal hydrated aluminum silicate, or the "clay substance" of common clays, varies in composition but is principally of the type, $Al_2O_32SiO_22H_2O$. Secondary in importance and amount are colloidal silicic acid, hydrated alumina, hydrated iron salts, and colloidal organic matter, plus small quantities of adsorbed soluble salts. Only small quantities of the pure mineral kaolinite, $Al_2O_32SiO_22H_2O$, are found as crystals in clays, and then mostly in the kaolin and china-clay types. Some clays, like those of the flint fire-clay type, are not plastic in the natural condition, but have been so treated by heat, pressure, or colloidal setting that fine grinding in water is necessary to restore the latent plasticity. If the colloidal content of the clay material predominates, as in bentonite, ball clays, or similar sticky, "fat," very plastic materials, a large amount of water is required for tempering, shrinkage is high and cracking prevalent. If the granular or non-plastic matter predominates, the clays are "short," "lean," and sandy with low shrinkage, and smaller contents of water are required for the best plastic condition. Commercial clay bodies have a nicely balanced ratio of colloidal to non-plastic material with the former acting as a thin film of both lubricating and friction producing medium around the inert granules.

Fineness of Clay Particles.—Nature, in all parts of the world and by the common weathering processes, has

[1] BLEININGER, A. V.: "Ceramic Processes Associated with Colloid Phenomena," *J. Ind. Eng. Chem.*, **12** (5), 436–438 (May, 1920); SCHLOESING: *Compt. rend.*, **79,** 376, 473 (1874); ROHLAND: *Z. anorg. Chem.*, **31,** 158 (1902); **41,** 325 (1904); CUSHMAN, A. S.: "The Colloid Theory of Plasticity," *Trans. Am. Ceram. Soc.*, **6,** 65 (1904); *Bur. Chem. Bull.* 85 (1904); *Bull.* 92 (1905); ASHLEY, H. E.: "Technical Control of the Colloidal Matter of Clays, *U. S. Bur. Standards Tech. Paper*, 23 (1913); FRANCE, W. G.: "An Ultramicroscopic Motion Picture Study of the Relation of Colloidal Content and Plasticity," *J. Am. Ceram. Soc.*, **9,** 67 (1926).

changed all kinds of rocks and minerals to the colloidal conditions. This is accomplished by disintegration, reduction in size, and an increase in the number of particles with the accompanying enormous increase in area of surface exposed. If the size of the particles decreases beyond a certain maximum (0.0001 millimeter), the colloidal condition is reached.

There is scarcely one of the silicate minerals that will not when sufficiently finely comminuted yield a substance possessing those

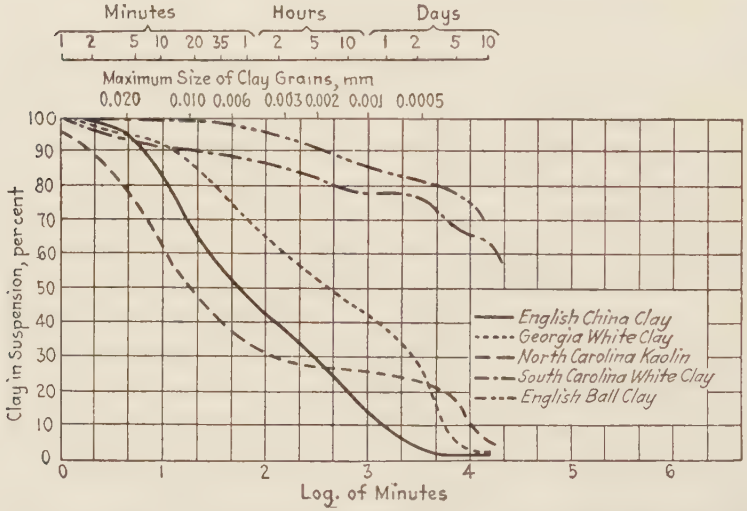


FIG. 10.—Size of clay particles determined by the plummet-sedimentation method. English ball clay has the highest percentage of the finest particles. (*Schurecht, H. G.: J. Am. Ceram. Soc.*, **4**, 818 (1921).)

peculiar physical properties of unctuous feel, plasticity, color, and odor, which are the only constant characteristics of the multitudinous and heterogeneous compounds known as clays.[1]

Schurecht[2] found that, by elutriation in water, from 68 to 98 per cent by weight of the particles in washed kaolins and ball clay from Georgia, South Carolina, and England, were smaller than 0.010 millimeter in diameter. By

[1] MERRILL: "Non-metallic Minerals," p. 221.

[2] SCHURECHT, H. G.: "Elutriation Tests on American Kaolins," *J. Am. Ceram. Soc.*, **3**, 355 (1920).

sedimentation tests, he[1] found that the following clays contained considerable percentages of particles whose maximum size was 0.0005 millimeter in diameter (Fig. 10):

	Per Cent
English ball clay	81
South Carolina kaolin	78
Georgia kaolin	28
North Carolina kaolin	22
English china clay	5

Bleininger[2] by elutriation methods found that from 40 to 99 per cent of fourteen different clays consisted of particles whose diameters were 5 microns[3] (0.005 millimeter) or less. By calculating the approximate size of particles from the rate of flow of water we find that Binns[4] separated from 58 to 71 per cent of particles, 1.1 microns (0.0011 millimeter) or less in size from five different kaolins.

Recent work by Jerome Alexander[5] using the ultramicroscope has shown that the Brownian movement is observed with practically every type of clay suspended in water, varying from the rapid motion of the finest particles to the more sluggish one of the aggregates or when hampered by the presence of flocculating electrolytes.

Bradfield,[6] using centrifugal forces of 30,000 times that of gravity, was able to separate 5.5 per cent colloidal material and 20.0 per cent by weight of clay particles varying in size from 0.4 to 1.2 microns, from a plastic Missouri clay.

If 45.3 per cent of the residual North Carolina clay, a comparatively coarse-grained, weakly plastic clay is com-

[1] Schurecht, H. G.: "Sedimentation as a Means of Classifying Extremely Fine Particles," *J. Am. Ceram. Soc.*, **4**, 812 (1921). Schramm, E., and E. W. Scripture, Jr.: "Particle Analysis of Clays by Sedimentation," *J. Am. Ceram. Soc.*, **8**, 243 (1925).

[2] Bleininger, A. V.: "The Effect of Preliminary Heating Treatment upon the Drying of Clays," *U. S. Bur. Standards, Tech. Paper* 1, 24 (1910).

[3] A micron equals 0.001 millimeter.

[4] Binns, C. F.: "A Comparison of Some Kaolins in Respect of Size of Grain," *Trans. Am. Ceram. Soc.*, **17**, 356–371 (1915).

[5] Alexander, J.: "Ultramicroscopic Examination of Some Clays," *J. Am. Ceram. Soc.*, **3**, 616 (1920).

[6] Bradfield, Richard: "The Chemical Nature of a Colloidal Clay," *Univ. Missouri Agr. Exp. Sta., Bull.* 60.

posed of particles whose diameter is 1.1 microns or less, a certain portion of these clay particles is undoubtedly in the colloidal field, that is, below 0.1 micron.

Colloidal Silica.—Silica, the most abundant oxide, may occur alone or in combination. It is found in combination with alumina both in the original hard rocks as complex aluminum silicates and in the clay forms as hydrous aluminum silicates. Natural plastic beds of silica do not occur, but instead comparatively pure silica is found in the hard form in large deposits: vein quartz, sandstone, or quartzite and beds of silica sands where the disintegration process has broken the structure but has not reduced the size to that of the colloidal condition. Quartz, the most common form, is one of our hardest minerals and consequently resists disintegration. In those cases, where the weathering processes have been severe and when accompanied by chemical activity, the colloidal forms of silica (silicic acid) have been formed. These usually do not survive but revert easily to the set gel condition and occur in the amorphous forms such as flint, chert, and chalcedony (see p. 15). Small amounts of silicic acid are found in plastic clays, and when present it increases the plastic strength and hardens with the clay mass on drying. Colloidal silicic acid particles are usually negatively charged. The potential difference has been found by Bradfield to be −0.030 volt. In acid solutions, however, silicic acid has been found to travel to the cathode. Stable colloidal solutions of silicic acid can be formed best by prolonged washing of sodium silicate. When quartz (Ottawa sand) was ground in a ball mill for 350 to 400 hours, Victor Lenher[1] found that 85 per cent of the material had a diameter of less than 0.004 millimeter, while 15 per cent was between 0.004 and 0.016 millimeter in diameter. The finest of the material, that which remained suspended in water for several weeks, showed rapid Brownian movements and the Tyndall cone effect, indicating that pure water alone will cause it to go into the colloidal state. Orthoclase was likewise converted to the colloidal condition by con-

[1] Lenher, Victor: *J. Am. Chem. Soc.*, **43**, 391 (March, 1921).

tinued grinding and water with but a small portion in true solution. This action of water on silica to produce a hydrated silica gel is accelerated by heat and pressure; under those conditions even large-sized crystals and fused quartz can be hydrated. W. Machaelis, in a paper read before the German Portland Cement Manufacturers on Mar. 9, 1909, stated that finely ground quartz will be converted into a colloidal hydrated silicic acid when boiled with water.

Colloidal Alumina and Various Colloidal Silicates.—Alumina, the second most abundant oxide, rarely occurs alone and is usually combined with silica to form one of the numerous hydrous silicates of alumina. The usual hydroxide form, bauxite, $Al_2O_32H_2O$, may be formed by more than one process.[1] It may occur in place as a residue from the decomposition of rocks; it may be found as a precipitate or in beds of transported material. The process by which aluminous silicates have been transformed into hydroxides, laterization, is still rather vague. The silica portion of a silicate is converted more readily to the colloidal form and removed in the presence of alkaline waters. The aluminum hydroxides thus represent an end-point in the decomposition of igneous rocks beyond that of the clays. In the recent studies of the separation of alumina from clays for the manufacture of metallic aluminum, the question of the state or condition of alumina in the so-called clay combination has arisen; some claim that a large part of the alumina is not present in a silicate combination but is already free. Edwards[2] found that 44 per cent of the number of analyses of clays in which both free and combined silica were determined showed an excess of alumina over that required to form kaolin. Laterization proceeds more rapidly in the tropics under alkaline conditions and lack of humus. Bauxite is found in the United States in Arkansas and Georgia, while diaspor, $Al_2O_3H_2O$, occurs in Missouri. By dehydration, bauxite passes into emery, and alumina crystallizes

[1] Clarke, F. W.: "The Data of Geochemistry," *U. S. Geol. Survey, Bull.* 616 (1916).

[2] Edwards, M. G.: "Occurrence of Free Alumina in Soils of the United States," *Econ. Geol.*, **9**, 112 (1914).

out of molten magmas as corundum. Bradfield[1] found that colloidal aluminum hydroxide possessed a high positive charge, giving a potential difference of +0.067 volt.

In a similar manner, various forms of iron, the third most abundant oxide, form *colloidal ferric hydroxide,* which increases the plastic content of red-burning clays. Ferric hydroxide is a positive sol, though it can be changed to a negative sol. It gave a potential difference of +0.030 volt.

The properties associated with plasticity of clays are similar to those associated with matter in the colloidal condition. The plastic and colloidal aluminum silicates, with their associated impurities, organic and inorganic, behave in many respects like the unquestioned colloids, such as silicic acid, ferric hydroxide, aluminum hydroxide, gelatine, glue, etc.,

> . . . in that they show the phenomena of hydrolysis, osmosis, adsorption, the ability to change reversibly from the gel to the sol form and *vice versa* in the presence of an excess of positive or negative ions, the property of shrinking in apparent volume down to a certain point proportionally to the loss of water, and the character of their dehydration and vapor-tension curves.[2]

Reversibility Factor of Colloidal Silicates.—The present conception of plastic clay consists of a colloidal substance of variable composition, complex hydrous aluminum silicates, with small amounts of hydrous silica, hydrous alumina, hydrous iron oxide, and water films, which surround the larger clay particles and non-plastic grains and bind the whole into a plastic mass which will remain plastic as long as the water is present. Such gelatinous colloidal substances, however, when prepared from other sources, have the property of setting to an irreversible condition on drying. Clays show only a tendency in this direction (see p. 137), and the bulk of the plasticity is not lost by drying, but is regained by rewetting. Bancroft[3] finds it necessary

[1] *Loc. cit.*

[2] Bleininger, A. V.: "Preliminary Heat Treatment of Clays," *U. S. Bur. Standards, Tech. Paper* 1, 3 (1910).

[3] Bancroft, W. D.: "Applied Colloid Chemistry," 1st ed., p. 155.

to introduce "some salt" into the theory, but cannot name the salt which will produce this reversibility. It is true that those clays, like the ball clays which approach kaolins in composition and yet are far more plastic, contain small quantities of organic material and salts like the sulphates which have been acquired during transportation. The humates and other organic salts may also play an important part, but this reversibility is common with those residual clays which do not contain the organic salts and cannot be directly connected with any salt impurity. The temperature of irreversible set varies with different colloids. Those clay materials more dependent on colloidal silicic acid or colloidal alumina will show a greater loss of plasticity on drying than those dependent on colloidal aluminum silicates, which do not become set until higher temperatures.

Development of Plasticity with Other Liquids besides Water.—Different dispersion media can mutually displace each other without destroying the colloid state. Graham was able to replace the water of a silicic acid gel with alcohol and with sulphuric acid. Spurrier[1] came to the conclusion that the hydroxide ion must be present to develop plasticity after obtaining negative results with carbon disulphide, benzene, carbon tetrachloride, ethyl alcohol, ether, bromoform, and sulphuric acid. Weak plastic and dry strengths were developed by Johnson[2] with glacial acetic acid, liquid ammonia, anilin, nitrobenzene, acetone, and benzol alcohol. Glycerine produces good plasticity for molding (plasticene), but the high viscosity of the liquid itself may give this property. Such glycerine plastic bodies resist drying. Of all the liquids other than water tried by Johnson, the greatest dry strength was produced by ammonia.

Relation between the Plasticity of Clay and Its Colloidal Content.—Clays are more plastic in the neutral and flocculated condition than in the deflocculated. Clays

[1] SPURRIER, H.: "The 'Why' of Ageing Clay," *J. Am. Ceram. Soc.*, **4**, 115 (1921).

[2] JOHNSON, HILDING: "Thesis: The Plasticity of Clay," University of Washington Library (1924).

composed of loosely cemented aggregates of fine-grained particles are more plastic than those composed of firmly cemented aggregates which do not disintegrate by agitation or those composed of crystalline particles.[1] The proportion of a clay which is readily deflocculated by alkalies does not usually represent all of the extremely fine clay particles, since a certain portion is ordinarily present in aggregates which are not affected by electrolytes and ordinary methods of dispersion. Flint fire clays represent the extreme case of resistance to disintegration by water. While the structure of a mass of ball clay breaks up on soaking and agitation in water, yet the clay particles will continue to remain together as loose aggregates unless the agitation and deflocculating action of electrolytes is continued for many days. Such masses of loose aggregates retain their plasticity after the deflocculated portions have been removed. On the other hand, some weakly plastic residual kaolins which have not been subjected to as much weathering activity as have the ball clays or plastic kaolins will retain but little plasticity when the fine suspended matter has been decanted.

Bole[2] gives the following conception of the mechanism of plasticity from the colloid standpoint. Plasticity is caused by the absorbed film of colloidal material which surrounds the clay grains, this film being of opposite polarity to the grain proper. The clay particles vary in size from the microscopic to submicroscopic to nearly molecular. The enveloping film is either amorphous or crystalline submicroscopic material. With the adsorbed film of positive polarity and the clay particle of negative electrical character, there is a neutral body[3] which is subject to the laws of attraction and repulsion. If the particle is small enough to possess a Brownian movement of sufficient amplitude, it will stay in suspension, and if not it will slowly settle.

[1] Schurecht, H. G.: "Note on the Relation of the Structure of Clay Grains to the Plasticity of Clays," *Bull. Am. Ceram. Soc.*, **1** (4), 153 (1922).

[2] Bole, G. A.: "Mechanism of Plasticity from the Colloid Standpoint," *J. Am. Ceram. Soc.*, **5** (8), 469 (1922).

[3] Neutral bodies would agglomerate from molecular attraction.

The frictional value of these adsorbed films is included in the plastic yield value of the clay-water system. The yield value is dependent upon the thickness of this surface film and can be regulated by the introduction of other charged bodies (electrolytes) of the proper electrical sign and in the proper amounts.

The addition of an electrolyte acting as a deflocculent causes the outer layer of film to be attracted to the ion of the same polarity as the clay particle, thus reducing the effective diameter and increasing the polarity of the plasticity-inducing particles. The clay particles which were in frictional contact through their adsorbed colloidal films are now no longer in contact and are actually repelling each other due to like and increased polarity. Viscosity falls because of the loss of friction between particles and because of this repulsion. A flocculating ion drives the action in the opposite direction, causing an increase in depth of the colloid film, thereby increasing the surface in actual contact and decreasing the repulsive force of plasticity-inducing particles. The maximum plasticity is developed with a given clay when the colloid films are the thickest.

Molecular Attraction. General Theory.—The attraction between the molecules of a solid or liquid is the binding force which holds the body together. Since a liquid so readily changes its shape, it is difficult to demonstrate the existence of such a force between the molecules of a fluid material. Berthelot in 1850 filled a glass tube with water at high temperatures and then sealed the tube; the water on cooling continued to fill the tube, without contracting and before it boiled, until it exerted a tensile force of 73.5 pounds per square inch upon the walls of the tube.[1] Alcohol and ether gave breaking strains of over 1,470 pounds per square inch, and they have been estimated as high as 2,800 atmospheres in the case of ethyl ether. This attraction between the molecules of a liquid is the force which must be overcome when a liquid is evaporated; and from

[1] EUCKEN, JETTE, and LAMER: "Fundamentals of Physical Chemistry," p. 152, McGraw-Hill Book Company, Inc. (1925).

the heat required for evaporation, it is found that the force produces a very great internal pressure across any imaginary plane in the liquid. Stefan and Temlirz obtained a value for alcohol of about 2,000 atmospheres. Budgett[1] found a maximum breaking strength of about 87 pounds per square inch for steel gages held together by a water film. On the assumption that the water occupied one-tenth of the surface, this gives a tensile strength of nearly 900 pounds per square inch for the water film.

The property of cohesion is illustrated by Swedish gages, which are pieces of hardened steel, the ends of which are so accurate and true that when two are carefully cleaned and placed together in such a manner as to exclude the air, they will cohere with a force as high as 35 pounds per square inch when tested in vacuum.

Such forces of molecular attraction are sensible only when the distances between the particles are exceedingly small. Thus, two molecules of water practically cease to attract when the distance between them exceeds a value that is roughly about 0.00005 millimeter.[2]

Molecular Attraction and Clay Particles.—If the particles of the dispersed phase are small enough to be in the colloidal condition, the forces of molecular attraction are active in (1) the water films, (2) between water films and the colloidal particles, and (3) between the colloidal particles.[3]

Grout[4] claims that the viscosity of the water film surrounding each small particle, not necessarily of colloidal dimensions, is greatly increased by the molecular attraction between the clay grains and water. By calculation he tries to prove that the amount of water required to produce such a film 0.00005 millimeter thick around each clay grain and to fill the pores between is about equal to the water usually added for tempering.

[1] *Proc. Roy. Soc.*, **82** *A*, 25 (1912).

[2] Duff, A. W.: "A Textbook on Physics," p. 146, P. Blakiston's Son and Company (1909).

[3] Chatley, H.: "Molecular Force and Plasticity of Clays," *Trans. Ceram. Soc.* (*England*), **19**, 1 (1919–1920).

[4] Grout, F. F., and F. Poppe: "Plasticity of Clay," *Trans. Am. Ceram. Soc.*, **14**, 71 (1912); *West Virginia Geol. Survey*, **3**, 26.

Purdy[1] claims that the salts which clay particles adsorb to their surfaces are the main factors in increasing the surface tension of the water films and in forming a viscous solution around the particles. Movement of grains is thus facilitated by this slippery medium, and flowage under pressure without rupture is permitted. He checks Grout's figures in regard to the weight of water films which will be molecularly attracted to clay particles (spherical) averaging 0.0005 millimeter in diameter. These will hold 22.5 per cent by weight of water (plastic basis) as films of 0.00005 millimeter in thickness.

Table XIV shows that the surface tension of the water films may be increased by the addition of various salts. Combinations of salts may magnify the increase.

For shales, the calculated weight of water films varied from 0.2 to 10.0 per cent (dry basis), the average being between 4 and 5 per cent. For softer clays such as alluvial and lacustrine clays which are disintegrated by the action of water alone, the molecularly attracted water will range from 10.0 to 17.7 per cent and with the finest clay materials over 25 per cent water. The weight of water required to fill the pore space should be added to these values, for they are lower than the amount of water required for tempering.

Fineness of Ground Shale.—The fineness of fresh shale grains is a direct function of the grinding received. Shales have been so compacted that water alone will not separate

[1] PURDY, R. C.: "Theory of Plasticity," *Trans. Am. Ceram. Soc.*, **11**, 555 (1909).

PURDY, R. C.: "Method of Calculation of Water Films," *Trans. Am. Ceram. Soc.*, **11**, 570.

a. Volume of clay sphere $\frac{\pi D^3}{6}$ where D is the mean diameter of the particles in each group separated by mechanical analysis.

b. Volume and weight of water films $= \left(\frac{\pi(D + 0.0001)^3}{6}\right) - \left(\frac{\pi D^3}{6}\right)$

c. Weight of dry-clay particles as given in mechanical analysis.

d. Total or collective volume of spheres in each group per unit volume = (weight given) ÷ (sp. gr. of the clay).

e. Number of spheres in each group per unit volume = (total volume of each group) ÷ (volume of clay sphere), or $\frac{d}{a}$.

f. Weight of the water film surrounding the spheres in each group of the sample (weight of water film) × (the number of spheres) or $b \times e$.

g. Sum of water required to give each particle in the total sample a film of water of the prescribed thickness. Sum of f's for each group.

the finest particles. By grinding in water, however, the structure of the grains is broken down and water will penetrate, so that the mechanical analysis will vary with the time and severity of the grinding treatment. Dry-pan grinding of shale produces plasticity, however, and the same grinding applied to an equally compacted sandstone will not make it plastic. The outer shell of these coarse shale particles should be considered as composed of loosely attached colloidal particles, which are gradually removed by friction and continued soaking in water. These provide a lubricated coating necessary for the movement of the particles on each other, sufficient for the stiff-mud, auger-machine practice common for shale products. When the plasticity of shales is increased by fine grinding, both the amount of water required for tempering and the shrinkage will be increased.

The force of molecular attraction, therefore, offers us a simple and yet fundamental theory of plasticity, without the entanglement of soluble salts or other factors which can be regarded as accessory and modifying in their activity. In the plastic condition, water films have separated the clay particles enough to weaken but not destroy the strong molecular bond of particle to particle. When the water films are removed by drying, the particles come into close contact and the strength increases in proportion to the intimacy of surface contact. The cohesion of the particles of a clay mass in drying and shrinking is strong enough to offset a considerable load; for example, the shrinkage of the bottom brick of a dryer car is accomplished under the load of the superimposed brick (see Chap. V, p. 140).

Surface Tension. General Theory.—Associated with the molecular attraction of particle to particle and particle to liquid film, we have the additional strength of the surfaces of these liquid films, and, being for the most part films, the "surface" forms a large part of the liquid mass. It is this force which under the term "capillarity" causes water to climb small vertical tubes and to penetrate into dry clay masses against the force of gravity. By measure-

ment, the surface tension of pure water at 20° C. is 0.077 gram per centimeter length of surface. This force decreases with the temperature but increases with the addition of most soluble salts. The surface tension of water is much larger than that of the other common liquids, with the exception of mercury.

The data in Tables XIV and XIV*A* show the surface tension for various liquids in contact with air. The surface tension of the liquid in contact with clay may be different. On the assumption that the surface tensions in contact with clay are at least in the same relative proportion, glycerine should give greater plastic strengths than the others save water if the surface tension is the controlling factor for plasticity. If mercury could be made to wet the clay surface, the plastic strength would be seven times that of the plasticity developed by water, on the same assumption. No definite relation can be drawn between the flocculation of clay suspensions with acids, the deflocculation with alkalies, and the change in surface tension of water by the addition of these electrolytes.

TABLE XIV.—SURFACE TENSION OF LIQUIDS[1]

(Liquids in Contact with Air)

Liquid	Temperature, degrees Centigrade	Surface tension, in dynes per centimeter
Water	0	75.6
Water	15	73.5
Water	100	61.5
Ethyl alcohol	15	22.2
Acetic acid	17	30.2
Amyl alcohol	15	24.8
Carbon disulphide	20	30.5
Chloroform	20	28.3
Ether	20	18.4
Glycerine	17	63.14
Mercury	18	520.0
Methyl alcohol	15	24.7
Olive oil	20	34.7
Petroleum	20	25.9
Turpentine	21	28.5

[1] Smithsonian Tables (1920).

TABLE XIV*A*.—SOLUTIONS OF SALTS IN WATER

Salt	Density	Temperature	Tension
$CaCl_2$	1.3511	19	95.0
	1.2773	19	90.2
HCl	1.1190	20	73.6
	1.0887	20	74.5
	1.0242	20	75.3
$MgCl_2$	1.2338	15–16	90.1
	1.1694	15–16	85.2
	1.0362	15–16	78.0
NaCl	1.1932	20	85.8
	1.1074	20	80.5
	1.0360	20	77.6
NH_4Cl	1.0758	16	84.3
	1.0535	16	81.7
	1.0281	16	78.8
K_2CO_3	1.3575	15–16	90.9
	1.1576	15–16	81.8
	1.0400	15–16	77.5
Na_2CO_3	1.1329	14–15	79.3
	1.0605	14–15	77.8
	1.0283	14–15	77.2
$MgSO_4$	1.2744	15–16	83.2
	1.0680	15–16	77.8

One pound per lineal inch equals approximately 175,000 dynes per centimeter.

W. D. Bancroft states that most salts increase the surface tension of the solution nearly proportional to the concentration, but that ammonia, nitric, hydrochloric, and hydrobromic acids lower it.

The Action of Water Films in Plastic Clays.—The particles of plastic clay are separated by continuous water films or liquid membranes. When the particles are moved with reference to each other, these liquid envelopes provide the means of lubrication and at the same time retard the movement because of their viscosity. When enough water is

added, a portion will be outside the attracted viscous layer, the mobility will increase, and the mass will be less coherent and more sticky. Still further increase of water produces a fluid wherein the particles come together only in frequent impacts.

Calculation of Plastic Tensile Strength of Clay from the Surface Tension of Water Films.—The surface tension alone of pure water will produce more than sufficient strength to explain the tensile strength of plastic clay. If we consider a cross-section of plastic English china clay having grains of varying size, but, for the sake of easy calculation, with square cross-sections, surrounded by water films 0.0002 millimeter thick we can determine the following:

TABLE XV

Per cent weight	Average diameter, millimeters	Number of particles per square centimeter	Length of film around each particle, millimeters	Total millimeter length of film per square centimeter	Percentage millimeters length of film
30	0.0002	277,778,000	0.0016	444,444	133,333
20	0.002	17,188,000	0.0088	151,254	30,251
5	0.0042	4,726,000	0.0176	83,178	4,159
15	0.0072	1,729,000	0.0296	51,178	7,677
10	0.0125	601,000	0.0508	30,531	3,053
20	0.0200	240,000	0.0808	19,392	3,878
Total millimeter length of film					182,351

73.5 times 18,235 centimeters equals 1,340,273 dynes per square centimeter.

Two-surfaced films would double their value. The above surface-tension value is that of water-air interface. The water-clay interface value may be different.

1,340,273 divided by 68,944 equals 19.4 pounds per square inch.

This same clay gives but 1.8 pounds per square inch plastic tensile strength when measured in the laboratory. Thicker water films, pockets of water and air, irregular shapes of grain, and variations of molding tend to reduce any theoretical value.

Adsorption of Liquids by Solids.—The interface or plane of separation between two phases is not an accurate plane if molecular sizes are used for comparison. When a liquid is in contact with a gas, the liquid has a slightly lower density just under the surface and the gas a slightly

greater density just above the liquid, than at greater distances from the plane of separation. The two phases are not then completely homogeneous within themselves at the interface. This action is not limited to phases of the same composition, for a gas or liquid of one composition may be adsorbed onto the surface of a solid of another composition. The thickness of the adsorbed layer may be only one molecule deep. If a liquid is adsorbed by a solid, it forms a film on the surface and is said to wet the solid. Water is adsorbed by clean glass, but mercury does not wet the glass nor come in contact with it save possibly under pressure. If a liquid wets a solid in the presence of air, it must first displace the layer of air adsorbed by the solid. Gum arabic adsorbs air so strongly that it is not readily wet by water. When a piece of porous earthenware is touched by the tongue, the force of the adsorption is felt as the water is sucked into the capillary pores and the air is driven out. Pressures of 3 to 4 atmospheres have been obtained when water penetrates porous chalk and plaster.[1] Spring[2] obtained pressures of $\frac{1}{5}$ atmosphere when air was displaced by water in contact with sand.

THICKNESS OF ADSORBED WATER FILMS

Maximum water film on German glass pearls[1]	128 millimicrons
Ten-mesh river sand[1]	285 millimicrons
Sixty-mesh river sand[1]	114 millimicrons

Water films on metals[2] may run as high as 100 microns in special cases.

[1] PETTIJOHN, J.: *Amer. Chem. Soc.*, **41**, 477 (1919).

[2] BANCROFT, W. D.: "Applied Colloid Chemistry, General Theory," p. 319 (1921).

Heat Developed by Adsorption of Liquids by Solids.—Parks[3] showed that approximately 0.00105 calorie per square centimeter of surface wetted was developed by water at 7° C. when brought in contact with silica, sand, or glass. Compare this with the "Pouillet Effect," Chap. IV, page 115.

[1] JAMIN, CHWOLSON: *Traite de physique*, **1** (III), 622 (1907); *Wied. Ann.*, **59**, 764 (1896).

[2] SPRING: *Mem. soc. belge geologie*, **97**, 13 (1903).

[3] *Phil. Mag.* (6) **4**, 247 (1902).

Selective Adsorption.—Hofman[1] showed that kaolin, calcium fluoride, gypsum, and barium sulphate have a much greater preference for water than for paraffine oil, amyl alcohol, carbon tetrachloride, benzene, or ether. White lead passes from water to linseed oil, because the white-lead particles offer a greater surface attraction to linseed oil than to water. In the Elmore bulk-oil process, certain sulphide ores can by shaking be made to pass from the water phase to the oil phase. The gangue remains with the water. Ash can be removed from ground bituminous coal by the use of oil and water. The ash goes to the water and the coal to the oil.

Adsorption of Dissolved Salts by Solids.—Adsorption is the accumulation of a dissolved substance upon the surface of the solid. Fuller's earth adsorbs the base from sodium chloride solutions so that the filtrate from the mixture gives acid reactions with litmus and phenolphthalein. Fuller's earth likewise gives an acid reaction when it is dampened and in contact with litmus, not because it is an acid material but because the earth adsorbs the base from the litmus. It is said that an acre-foot of fuller's earth as solid would adsorb 30,000 pounds of lime.[2]

Geller and Caldwell[3] found that the following amounts of NaOH were completely adsorbed by kaolins without showing the presence of free alkali sufficient to color phenolphthalein:

North Carolina kaolin	0.125 per cent dry weight of clay
Georgia kaolin	0.100 to 0.125 per cent dry weight of clay
Florida kaolin	0.225 to 0.250 per cent dry weight of clay

They use the term "absorption" to designate the removal from solution of a dissolved substance by a solid, regardless of the mechanism by which it occurs. This may be done

[1] HOFMAN: *Z. phys. Chem.*, **83**, 385 (1913).

[2] BANCROFT: *loc. cit.*, 1st ed., p. 121.

[3] GELLER, R. F., and D. R. CALDWELL: "The Absorption of Sodium Hydroxide by Kaolins," *J. Am. Ceram. Soc.*, **4**, 468 (1921).

by chemical action, which very probably occurs with clays when the concentration of alkali or acid is large, by solid solution, or by physical adsorption of the salt upon the great surface of the dispersed phase. Figure 11 shows the effect of a solution of sodium hydroxide upon the pH value of pure water and upon two clay suspensions. A portion of the alkali is removed by the suspended clay. Freund-

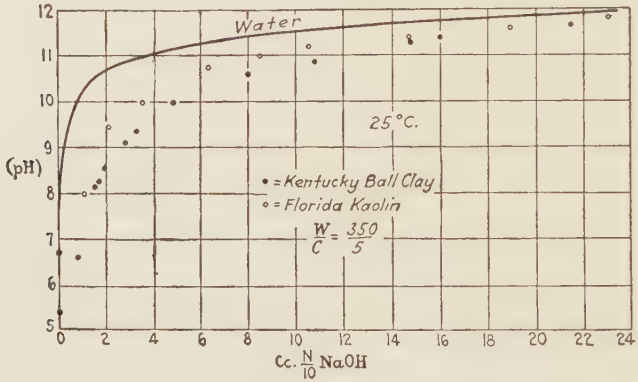


FIG. 11.—The removal of alkali from solution by a clay in suspension. (*Hall, F. P.: J. Am. Ceram. Soc.*, **6**, 996 (1923).)

lich has used an equation expressing the relation between the amount of material adsorbed and the quantity of adsorbent:

$$\frac{x}{m} = (KC)^{1/n}$$

In the equation x is the amount of salt adsorbed in grams by m grams of absorbent, and C is the concentration in the solution after adsorption. The value of K is an index of the degree of subdivision of the dispersed phase as shown in the following data by Hall[1] for different clays:

[1] HALL, F. P.: "Effect of Hydrogen-ion Concentration upon Clay Suspensions," *J. Am. Ceram. Soc.*, **6**, 998 (1923).

TABLE XVI.—TABULATION OF CLAYS IN ORDER OF DESCENDING VALUE OF K

Clay	K	$1/n$
1. Bentonite	0.89	0.58
2. Kentucky ball clay (4)	0.107	0.27
3. Florida kaolin	0.089	0.33
4. German ball clay	0.080	0.29
5. Tennessee ball No. 3	0.056	0.16
6. North Carolina kaolin	0.047	0.21
7. Delaware kaolin	0.036	0.26
8. English china *J.R.* 3	0.032	0.26
9. Georgia kaolin	0.017	0.15
10. South Carolina kaolin	0.015	0.14
11. Lee Moor English china	0.012	0.19

The original content of adsorbed salts will modify the amount of salt adsorbed by the clays. Such may be the cause of the Georgia kaolin, which is considered to be a finely divided clay.

Like fuller's earth, clays will adsorb an appreciable amount of the basic ion of common salts like NH_4CL, $BaCL_2$, $AL_2(SO_4)_3$, and $CuSO_4$, but practically none of the acid ion.[1] Ashley (Chap. IV, p. 118) used the adsorption powers of clay in testing its plasticity. The large complex molecules of malachite green or methylene blue are adsorbed in amounts corresponding to the colloidal nature and content of the clay mass.

Clay Soap.—Some clays possess such a highly colloidal nature that they resemble soap in both lathering and detergent properties.[2] Both have surface tensions lower than that of water, greater viscosity than water, emulsifying properties, and power to absorb dirt and grease. It is reported that clay is being mined in California for use as soap in laundry work.[3]

The Ageing of Clays and the Effect of Organic and Bacterial Action on Plasticity.—The ageing of clay in the

[1] SULLIVAN: *U. S. Geol. Survey, Bull.* 312; CUSHMAN: *Bur. Chem. Bull.* 92; BLEININGER, A. V.: "Ceramic Processes Associated with Colloid Phenomena," *J. Ind. Chem. Eng.*, **12**, No. 5, 436 (1920).

[2] WESTON, F. E.: "British Clayworker," **28**, 245–246 (1920).

[3] *J. Am. Ceram. Soc.*, **4**, 941 (1921). German patent.

plastic condition has a remarkable effect on its plasticity. This is especially true in the case of the weakly plastic, artificial pottery bodies containing a large percentage of non-plastic material such as feldspar and flint. The fresh body will be difficult to work without tearing and cracking. The aged body will be tougher and smoother, will flow more easily under the tool, and will give less cracking. Riddle and McDanel,[1] by ageing a porcelain body for 8 months in the plastic condition, increased the dry transverse strength from 139.8 to 267.6 pounds per square inch. Kaolin bodies were made stronger than unaged bodies containing 16 per cent ball clay. The aged bodies vitrified at somewhat lower temperatures, their shrinkage was less, the ware burned more uniformily and had a better firing range.

The ageing of bodies containing indurated or hardened grains of shale, fire clay, or even the agglomerations of ball-clay particles permits a greater penetration of water into these particles. This dissociation causes an increase in plasticity. Unweathered shale grains will swell with the absorption of tempering water after the ware is molded and will cause local points of cracking and disturbance. Ageing of the plastic clay likewise gives the air which has been entrapped during pugging a chance to escape or to be better distributed throughout the mass.

The ageing effect is magnified or hastened if gums, tannin compounds, humus, or similar organic materials have been added. It is believed that the improvement is due in part to the formation of organic acids caused by the bacterial action and chemical processes. The speed of the reaction depends on the growth of the bacteria and hence is greatest when their living conditions are most comfortable. Temperatures between 80 and 90° F. are favorable. When oxygen is added in the form of H_2O_2 or an abundance of other food is provided, their growth is hastened. As this fermenting action progresses, carbon dioxide, hydrogen sulphide, etc. are evolved while the strength and toughness

[1] Riddle and McDanel: "Some Types of Porcelain," *J. Am. Ceram. Soc.*, **1**, 617 (1918).

increase. It has been suggested that the bacteria may produce a better working structure by absorbing the entrapped air and better distributing their gases. Carbon dioxide alone will reduce the plasticity of a clay.[1]

Besides the reputed bacterial action, there is found the direct and quicker action of the organic materials themselves, those named above together with liquor from steamed tan bark, steamed straw, catechu, etc. When the action is immediate, it is apparently a case of change in dispersion of the colloidal clay particles. Otherwise, some of these materials may merely act as a food supply and hasten bacterial growth.

It has been frequently observed that of two similar clays the stronger and more plastic will have the greater organic content. The plasticity is not primarily dependent upon this organic content, however, even though it does increase the original plasticity value. Clays which have never come in contact with organic materials have plasticity; this property cannot be destroyed by the removal of organic constituents from other clays. Hamor and Gill[2] added the organic extractives, ethyl alcohol, commercial benzol, acetone, and carbon tetrachloride to several clays and reduced the plasticity values by 6.2 to over 50 per cent.

Bacterial and Organic Action in Glazes.—Fritted glazes, containing but a small percentage of plastic material, will settle rapidly to a dense mass in the bottom of the container. After ageing in the presence of gums and especially in the acidic condition, fermentation will develop and this settling

[1] Stover, E. C.: "Bacterial Growth as a Factor in Ageing Clay Mixtures," *Trans. Am. Ceram. Soc.*, **5**, 358 (1903). Keepler, G., and A. Spangenberg: German patent 201404, 80 *b* (Aug. 29, 1906). Watts, A. S.: *Trans. Am. Ceram. Soc.*, **6**, 52 (1904). Acheson, E. G.: "Egyptianized Clay," *Trans. Am. Ceram. Soc.*, **6**, 31 (1904). Minton, L. H.: "Tests of the Acheson Process," *Trans. Am. Ceram. Soc.*, **6**, 231 (1904). Gates, W. D.: *Trans. Am. Ceram. Soc.*, **6**, 48 (1904). Spurrier, H.: "The Why of Ageing Clay," *J. Am. Ceram. Soc.*, **4**, 113 (1921). Wahlin, J. G.: "Bacterial Growth in Enamel Slip," *J. Am. Ceram. Soc.*, **7**, 160 (1924).

[2] Hamor, W. A., and H. E. Gill: "On the Effect of Extraction upon the Plasticity of Clay," *J. Am. Ceram. Soc.*, **2**, 593–601 (1919).

will be greatly retarded. The color will be darker, and the glaze slip will feel slimy instead of granular and watery. The odor is likely to be offensive. Underslips containing large percentages of clay matter and gum will rapidly ferment, develop gas, and show an increase in plasticity, which is revealed by greater smoothness, covering power, and ease of spraying. The offensive qualities can be overcome by such disinfectants as formaldehyde. Gums are commonly added to underslips and glaze coatings to increase the dry mechanical strength and to avoid physical defects such as pinholes and small cracks.[1] Care must be exercised in the use of such materials. The increase of the colloid content causes greater shrinkage with the accompanying danger of cracking and warping. When the materials are soluble in water, they will collect on the surface in drying, leaving the interior weak and producing a crust to which glases adhere with difficulty.

4. Non-plastics. Shape, Size, and Distribution of Sizes of Grain

Purpose and Composition of Non-plastics.—Two distinct and yet merging portions of our commercial clay bodies are recognized: the cementing or plastic portion and the non-plastic or granular portion. The former has been discussed under Colloids. The plastic portion contains among its coarser sizes, particles which cannot be caught by the ordinary methods of screening and yet do not contribute to the plastic strength. Very fine quartz grains from 50 to 10 microns in diameter are typical examples of these fine non-plastics which dilute the plasticity.

Non-plastics consist of the natural mineral impurities such as a quartz, feldspar, mica, limestone, pyrites, augite, hornblende, etc., and artificial materials such as the calcined and ground "grog" commonly used in commercial terra

[1] Wilson, Hewitt: "Pinholing and Peeling of Terra Cotta," *Trans. Am. Ceram. Soc.*, **19**, 209 (1917).

cotta and fire-brick bodies and ground feldspar and flint of whiteware bodies. Without the non-plastic portion, it would be impossible to shape, dry, and fire commercial wares because of excessive stickiness, high content of water, high shrinkage, difficulty of removing water, and a great tendency to crack. Consequently, the granulometric characteristics of the non-plastics are important. The amount, and the maximum and minimum size of grain, with the proper adjustment of sizes and shape of grain, must be selected and maintained for various products and purposes.

Surface Factor.—It is customary with some to calculate a numerical value called the "surface factor," which varies with the amount of surface exposed by the non-plastic portion of the mass. The surface is the portion which must be covered by the cementing substance for plastic strength and it is the amount of surface exposed which influences the progress of vitrification and fusion. The colloidal sizes of clays have not been measured accurately, and hence this causes considerable error in calculating the surface factor of a plastic clay. The calculation of the surface factor forms a convenient method for summarizing or comparing the mechanical analyses obtained by screening or elutriation tests. The diameters of all the sizes can be measured under the microscope with the exception of those passing the last elutriation can into the overflow (Watts' apparatus). This may produce considerable error, for in some clays like the ball clays, this portion may be over 90 per cent of the total (see Chap. IV, p. 80). A more recent method consists of determining with an electroscope the relative amounts of the radioactive substance, thorium *B*, which is adsorbed onto the surfaces of powdered materials after the proper treatment. It is necessary to prepare an adsorption curve for each material.[1]

The surface factor gives greatest service in estimating the properties of the non-plastics, feldspar, and flint in

[1] KOEHLER, W. A.: "Determination of the Relative Surface Areas of Powdered Materials," *J. Am. Ceram. Soc.*, **9**, 437 (1926).

TABLE XVII.—THE PROGRESSIVE SUBDIVISION OF A CUBE[1]

Length of edge	Number of cubes	Total surface
1 centimeter 0.3937 inch	1	6 square centimeters 0.93 square inch
1 millimeter 0.0394 inch	1,000	60 square centimeters 9.3 square inches
0.1 millimeter 0.0039 inch	1,000,000	600 square centimeters 93 square inches
0.01 millimeter 0.0004 inch	1,000,000,000	6,000 square centimeters 930 square inches
1 μ 0.001 millimeter	1,000,000,000,000	6 square meters 212 square feet
0.1 μ 0.0001 millimeter	1,000,000,000,000,000	60 square meters 2,118 square feet
0.01 μ 0.00001 millimeter	1,000,000,000,000,000,000	600 square meters 21,274 square feet
1 $\mu\mu$ 0.001 μ	1,000,000,000,000,000,000,000	6,000 square meters 211,740 square feet
0.1 $\mu\mu$ 0.0001 μ	1,000,000,000,000,000,000,000,000	6 hectares 14.83 acres
0.01 $\mu\mu$	1,000,000,000,000,000,000,000,000,000	60 hectares 148.26 acres
0.001 $\mu\mu$	1,000,000,000,000,000,000,000,000,000,000	6 square kilos 1482.6 acres or 2.3 square miles

[1] ALEXANDER, JEROME: "Colloid Chemistry," 15, D. Van Nostrand Company (1919).

whiteware bodies and the coarse grogs in terra cotta, saggar, and fire-brick bodies.[1]

Purdy's Method for Calculating Surface Factor.[2]—The surfaces per unit volume of spheres and cubes vary inversely as their diameters.

1. Determine the average diameter of each group of sizes.
2. Determine the surface factor for each group by inverting the mean diameter of each group.
3. Multiply the surface factor of each group by the percentage weight of the group.
4. The surface factor of the entire sample equals the sum of all the results of No. 3 or the sum of the percentage surface factors.

Increase of Surface Area with Grinding.—Finer grinding or reducing the size of particles accompanied by the increase in their number develops a remarkable increase in the surface area, as shown in Table XVII.

It is apparent that a given quantity of plastic material, just capable of coating a given number of coarse non-plastic particles, may prove insufficient to cover the surface of the same volume of non-plastic particles if they are ground to a finer condition.

Fineness Modulus.—Duff A. Abrams[3] has suggested a *fineness modulus* to replace the older sieve-analysis curve for proportioning concrete aggregate. It is the sum of the percentages given by the sieve analysis, divided by 100, sieving from the 100-mesh to the 1½-inch size, as follows:

[1] KIRKPATRICK, F. A.: "Modulus of Rupture and Surface Factor," *Trans. Am. Ceram. Soc.*, **19**, 271, 294 (1917).

[2] PURDY, R. C.: "Calculation of Comparative Fineness of Ground Materials by Means of a Surface Factor," *Trans. Am. Ceram. Soc.*, **7**, 441 (1905). MELLOR, J. W.: "Jackson's and Purdy's Surface Factors," *Trans. Ceram. Soc.* (*England*), **9**, 94 (1909–1910).

[3] ABRAMS, DUFF A.: "Design of Concrete Mixtures," Structural Materials Research Laboratory, Lewis Institute, Chicago, *Bull.* 1, 5 (1921).

TABLE XVIII

Sieve	Medium sand	Coarse pebbles
Plus 100 mesh	91	100
48	70	100
28	46	100
14	24	100
8	10	100
4	0	100
⅜ inch	0	86
¾ inch	0	50
1½ inch	0	0
Fineness modulus	2.41	7.36

Proportioning the Non-plastic Aggregate.—As in lime and cement concrete mixtures, a certain analogy exists between the ratio of sizes of the aggregate and the density and strength of the clay mixtures. The relation has not been clearly established in clay bodies containing large percentages of plastic shrinking material because the plastic mass more than fills the voids of the aggregate. Hence, too close a comparison cannot be drawn between the proportioning of concrete aggregate and the sizing of grog for the ordinary clay body. In the former, the aggregate is usually coarser (gravel and sand), the mixture is far less plastic, the cementing portion does not shrink so much as plastic clay in the development of its strength, and concrete is not fired while clay is hardened by partial fusion. Comparisons can be drawn between concrete mixtures and such special products as silica, sillimanite brick, or other refractory materials which contain only a small per cent plastic material when molded.

The pore space in an aggregate will depend on the ratio of sizes, the shape, and the arrangement of the particles. For spheres of equal diameter, the volume of pore space will be about 48 per cent of the total volume for cubical piling and nearly 26 per cent for hexagonal piling. More plastic clay will be needed to fill the pore spaces and coat

a mass of particles having approximately equal size than graded sizes. In such mixtures, shrinkage occurs until the large grains touch. After that, the plastic portion of the mass continues to shrink between the grains and may crack either in drying or firing. This increases the internal pore space and causes a rough exterior surface due to the projection of the non-plastic grains, between which lie concave surfaces of the plastic medium. Such a condition is seen in poorly balanced refractory and terra cotta bodies in which comparatively coarse grog is used.

If the plastic or cementing portion only acts as a film on the surfaces of the aggregate, the greatest density is obtained by using the maximum quantity of maximum-sized pieces and filling the voids with small particles of such size that they do not crowd or elbow the larger grains out of their most compact arrangement. The intermediate sizes must be removed. The small particles should be the maximum for their position, and, in turn, their void spaces should be filled with smaller particles, etc., until finally the size of the plastic or cementing particles is reached. The common grinding processes produce a gradation of sizes, each of which elbows the next larger out of its most compact arrangement. Although the following does not represent the maximum density, an illustration of a compact structure is shown by the mechanical analysis used for mullite brick: 50 per cent by weight, 2 to 4 mesh; 40 per cent by weight, minus 20 mesh; 10 percent by weight, plastic bond clay.

This mixture must be tamped until the 2- to 4-mesh particles have been pounded into the most compact structure with the finer material occupying only the interstices (Fig. 12).

If the fired body is dependent primarily upon the fired strength of the plastic portion, any foreign, non-reacting, non-plastic material will dilute this strength in proportion to the amount added. Refractory grog added to a less refractory clay will decrease the fired strength of the clay because the clay cannot grip or adhere to the surfaces of

the grog grains so well as it coheres within itself. Usually, in such cases, the more refractory grog is weaker than the same volume of fired clay. On the other hand, if the non-plastic grains have a lower softening point than the clay, they may dilute the plastic and dry strength, but will add to the fired strength, because they become the cementing

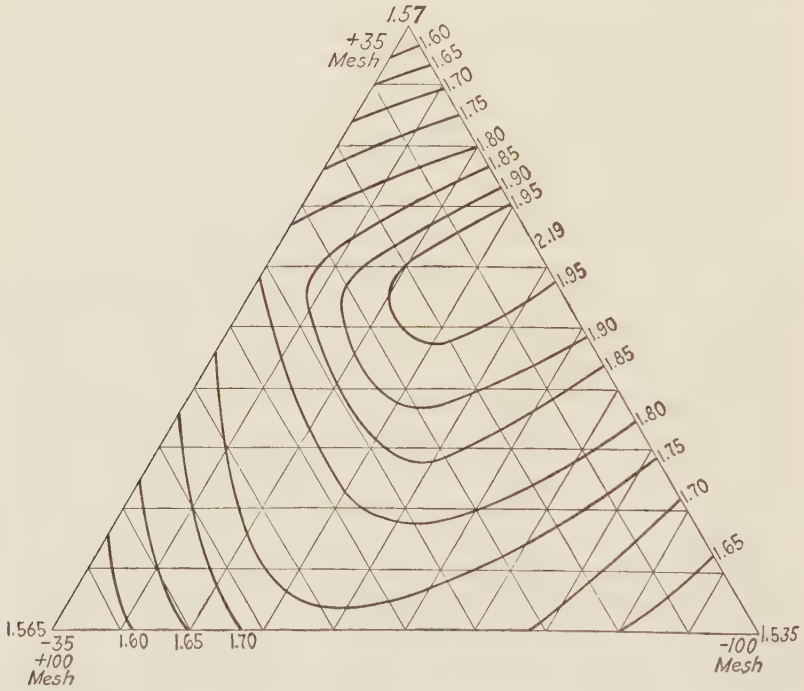


FIG. 12.—Bulk specific gravity of mullite grog grains determined by jarring in a graduate.

medium at the high temperatures. This is the case of feldspar in a whiteware body. At high temperatures, sillimanite, corundum, and silicon carbide will likewise provide strength in refractory brick by developing an interlocking, crystalline framework, which replaces the colloidal strength of bonding agents used during the dry and early fired periods.

5. The Measurement of Plasticity

The following outline represents the different methods which have been suggested for the measurement of plasticity of clays:

Direct Methods

a. FORCE AND DEFORMATION.

1. Hand working.
2. Measurement of force and resulting deformation.

Indirect Methods

b. TEMPERING WATER.

3. The amount of tempering water or water of plasticity necessary to bring the clay to its best working consistency.
4. The range of water of plasticity necessary to change the condition of the clay from the dryest working state to the wettest or the flowing state. (Atterberg plasticity number.)
5. The ability of the clay to retain its tempering water when in contact with a porous surface.

c. DRYING SHRINKAGE.

6. The amount of dry-volume shrinkage.

d. WATER ADSORPTION.

7. The amount of water adsorbed by the dried clay under regulated humidity conditions.

e. STRENGTH.

8. The plastic tensile strength.
9. The dry tensile strength or dry transverse strength with or without the admixture of non-plastics.

f. VISCOSITY OF CLAY SUSPENSIONS.

10. The amount of water required to impart a definite viscosity to the clay with or without flocculents or deflocculents.

g. MEASUREMENT OF COLLOID MATTER.

11. The amount of malachite green or other salts adsorbed by the colloidal material.
12. The percentage weight of particles possessing colloidal dimensions and properties. The possible separation of the colloidal-size particles from the larger sizes by elutriation or selective settling methods, ultrafiltration through several selected membranes having openings of definite sizes, or by selective supercentrifuging.

Force and Deformation. *a. Hand Working.*—The hand-working or hand-feel method is an estimation of the plasticity of the clay compared to an ideal plastic condition, varying with the type of clay body with which the operator is experienced. It combines tensile strength, ductility, ability to stand stresses of tension, torsion, and compression without rupture and with easy deformation. This is the

oldest method and the one in common commercial use at the present time. It enables one with no apparatus to sort clays into several groups which can be checked only in a general way by other operators.[1] It gives no numerical data, but to an experienced operator is accurate enough for most ceramic control work.

b. Measurement of Force and Resulting Deformation.— According to the definition for plasticity given in Chap. IV, page 55, it is necessary to measure both the yield value and the mobility. When these are found, there still is no numerical relationship between them to determine a value for plasticity. A comparison of the plasticity of two different clays can be made, however, by so varying their properties that they have either the same yield value or the same mobility. The more plastic will have the greater yield value or the higher mobility. The yield value can be varied by changing the water content and the mobility by additions of suitable non-plastic material such as potter's flint. Very plastic clays require a large amount of water not only to bring them to an easily workable mass but likewise to change them from the plastic condition to the fluid or flowing condition. Powdered, non-plastic grains, such as potter's flint, will remain as incoherent sand until but a very slight excess of water not only gives a slight, feeble plasticity but almost at the same time changes them to the fluid condition.

The measurement of the yield value and mobility can best be made with the Bingham-Green plastometer,[2] which is simply a modification of the flow type of viscosim-

[1] Bole, G. A.: "Mechanism of Plasticity from the Colloid Standpoint," *J. Am. Ceram. Soc.*, **5**, 474 (1922).

[2] Green, H.: "Further Development of the Plastometer and Its Practical Application to Research and Routine Problems," Proceeding *Am. Soc. Testing Materials*, **20** (II), 451–494 (1920); Hall F. P.: "Methods of Measuring the Plasticity of Clays," *U. S. Bur. Standards, Tech. Paper* 234 (1923); *J. Am. Ceram. Soc.*, **5**, 346 (1922) and **5**, 916 (1922); Bingham, E. C.: "Discussion of Plasticity," *Bull. Am. Ceram. Soc.*, **3**, 375 (1924); Bingham, E. C.: "Plasticity as a Means of Control of Properties," *J. Am. Ceram. Soc.*, **7**, 430 (1924); Cooke, R. D.: "The Plastic Properties of Enamel Slip," *J. Am. Ceram. Soc.*, **7**, 651 (1924).

eter. The latter has been used to determine the viscosity of clay slips for a long time. In reality it measures the mobility of clay suspensions in which a large amount of water has produced such a low yield value that the small pressure of the weight of the slip alone is necessary for movement. The plastometer, however, is made suitable for plastic clays and heavy pastes by the following developments: (1) there is an externally applied air pressure which

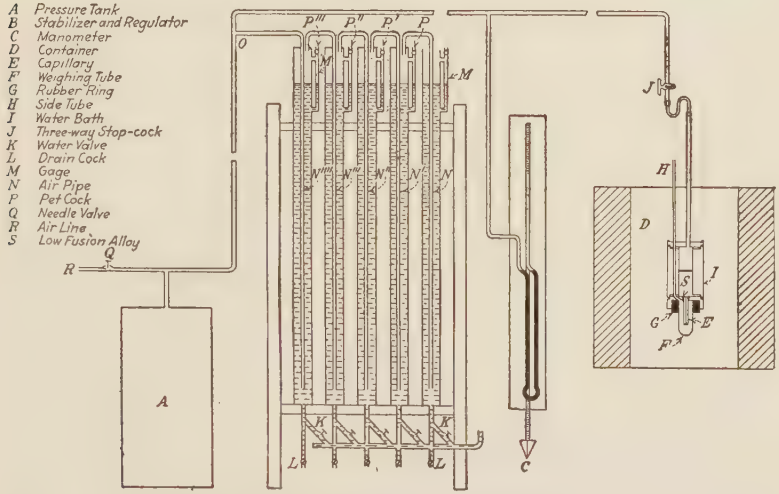


FIG. 13.—The Bingham-Green plastometer. (*Bingham, E. C., and Henry Green: Proc. Am. Soc. Testing Mat.* (1919).)

is capable of accurate measurement; (2) the ratio of the length of tube to diameter is of a higher order of magnitude; and (3) the velocity of flow can be regulated so that the kinetic-energy correction becomes negligible. The principal parts are: a container for the material to be tested with a capillary at the lower end; a compressed-air system for applying pressure, which includes a large air reservoir and a stabilizer for maintaining a constant pressure; and a flowmeter to measure the rate of flow of the substance as it is forced through the capillary (Fig. 13).

Modifications of this elaborate and costly apparatus can be made by the use of the high gas pressures of oxygen or carbon dioxide in the ordinary storage tanks and their

accompanying regulating valves together with a simple chamber and orifice. Such an apparatus can be used only for comparative purposes and not for absolute values. The yield value or the pressure required to start the flow through a given orifice can be determined. Either the mobility (rate of flow per unit of pressure from which the yield value has been subtracted) or the weight of the thread produced through the orifice before the tensile strength of the clay has been exceeded can be found.[1] The latter will vary with the die working ability of the clay or the ability of the clay to form a smooth, continuous column without irregularities which would cause cracks and other weak places. According to the original definition of plasticity there must be continuous deformation without rupture.

Stringer and Emory Ball Deformation Test.[2]—A sphere of plastic clay, 2 centimeters in diameter, is placed on a glass plate beneath a piston of which the vertical movements can be measured. Sufficient fine shot is allowed to flow into a bucket at the top of the piston to cause it to descend and deform the sphere until it cracks. In this manner a relation is obtained between the amount of deformation and the resistance the clay offers to a change in shape. It would be supposed that in a great many instances no cracking of the clay would take place, particularly with very plastic clays and with increased amounts of water. F. P. Hall[3] states that this method is unsatisfactory because it is difficult to obtain concordant results.

The Emley Plasticimeter.[4] (Fig. 14.)—This instrument has been used for testing clays although it was developed to

[1] Stover and Lindley: "A Note on the Measurement of Plasticity and Tensile Strength," *Trans. Am. Ceram. Soc.*, **7**, 397 (1905).

[2] Mellor, J. W.: "On the Plasticity of Clay," *Trans. Ceram. Soc. (England)*, **21**, 93, 94 (1921–1922).

[3] Hall, F. P.: "The Plasticity of Clays," *J. Am. Ceram. Soc.*, **5**, 346 (1922).

[4] Emley, W. E.: "An Instrument for Measuring Plasticity," *Trans. Am. Ceram. Soc.*, **19**, 523 (1917); Kirkpatrick, F. A., and W. B. Orange: "Tests of Clays and Limes by the Bureau of Standards Plasticimeter," *J. Am. Ceram. Soc.*, **1**, 170 (1918); *U. S. Bur. Standards, Tech. Paper;* Cox, Paul E.: "A Study of Plasticity by Practical Potter's Methods," *J. Am. Ceram. Soc.*, **7**, 151 (1924).

determine the plasticity of limes and wall plasters and to measure the forces similar to those actuating a trowel as it spreads plaster onto a wall.

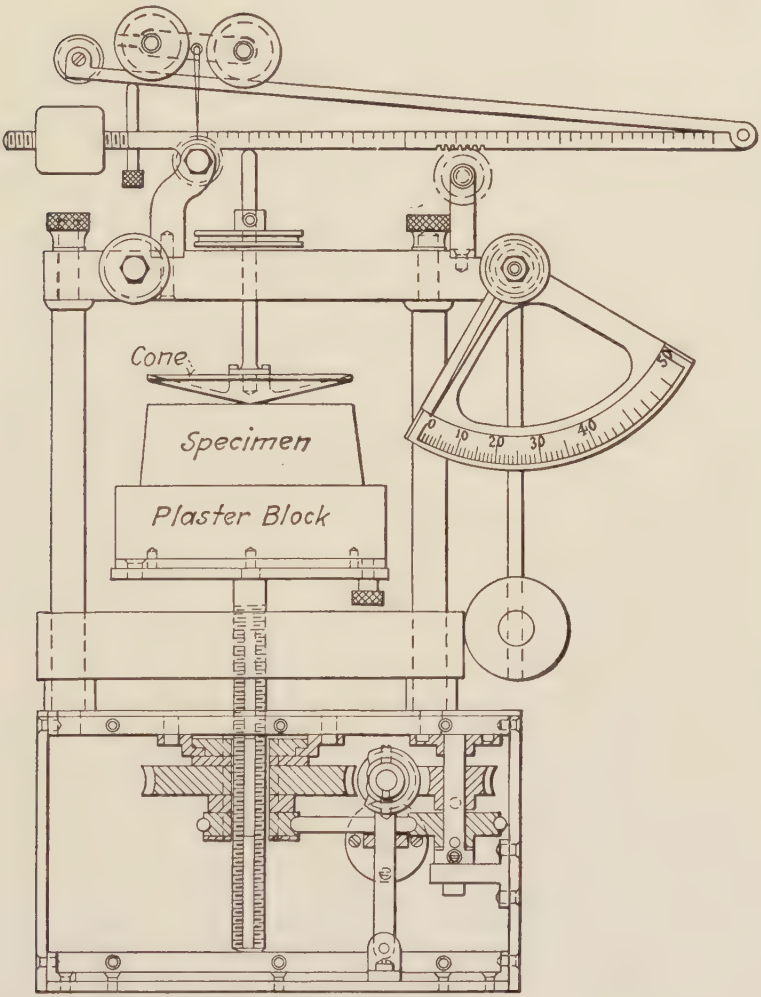


FIG. 14.—The U. S. Bureau of Standards plasticimeter. (*Emley, W. E.: Trans. Am. Ceram. Soc.*, **17**, 526 (1917).)

For clay testing, a specimen of the plastic clay ¼ inch thick is placed on a porous plaster of paris disk of known and constant absorption. This is mounted on the upper end of a vertical shaft, directly below and concentric with a flat, metal disk. The shaft is threaded and runs through a fixed nut.

As the shaft revolves, the clay is forced against the metal disk with a spiral motion. The metal disk is so mounted that any motion is transmitted through a system of levers to a bar, which is caused to swing out of its originally vertical position. The greater the angle through which the bar is moved, the greater will be the force of gravity tending to return it and the metal disk to their original position. It follows, therefore, that if a constant force tends to cause motion of the metal disk, the bar will swing out until the force of gravity acting on the bar is in equilibrium with the force acting on the metal disk. When this condition has been attained, both the cone and the bar become stationary, and the force acting on the metal disk is directly proportional to the sine of the angle through which the bar has moved. The bars are graduated and provided with bobs which can be moved up or down, thus decreasing or increasing the force required to produce a given angular deflection. The average relative tangential force for the first 5-minute period is called the "plasticity figure" of the clay. The clays were ground to pass a 100-mesh sieve and tempered with sufficient water to produce a consistency equivalent to that necessary for pottery jiggering. As the water is absorbed by the plaster, the viscosity of the paste increases, and the force becomes greater at a rate depending upon the rate of absorption. The results show that the relative behavior of the clays in jiggering appears to be indicated by the data obtained with this instrument. The action of the jiggering tool in pressing the clay against the plaster mold is quite similar to that of the metal disk in pressing the clay against the plaster base.

TABLE XIX.—PLASTICITY FIGURES FROM THE EMLEY PLASTICIMETER

Tennessee ball clay	0.397
Kentucky ball clay	0.561
Illinois "kaolin"	0.567
Maryland kaolin	0.600
Florida kaolin	0.682
Georgia kaolin	0.790
New Jersey fire clay	0.879
North Carolina kaolin	0.992
English china clay	1.120
Delaware kaolin	1.370
Porcelain bodies	0.830 to 1.050

This test considers that the property of retaining water and resisting deformation are measurements of plasticity.

Tempering Water. *Atterberg Plasticity Number.*[1]—This method was developed by Albert Atterberg,[1] but tested by C. S. Kinnison of the United States Bureau of Standards.[2] It is based on the assumption that plasticity varies as the range in water content of the workable body, the more

[1] ATTERBERG, ALBERT: *Intern. Repts. Pedology* (1911).

[2] KINNISON, C. S.: "A Study of the Atterberg Plasticity Method," *U. S. Bur. Standards, Tech. Paper* 46, 3. (1915.)

plastic clays possessing a greater range. As water is added to pulverized dry clay, the mass first assumes a damp powder condition, in which it can be made to hold together by strong pressure. As the water content increases, the amount of pressure required for cohesion is lower, until the best working condition is reached, after which it passes into a sticky state and finally is unable to hold its own shape and becomes a fluid "slip." Clay wares are shaped while the clay is in one of four different degrees of consistency:

1. Dry pressing of brick and tile with pressures of 5 to 6 tons per square inch in hydraulic or cam presses.

2. "Stiff-mud" shaping with auger machines and dies to produce a column of stiff clay for brick, tile, sewer pipe, etc. The column is pushed through a hollow die by a plunger or screw. Stiff-mud brick may also be re-pressed.

3. "Soft-mud" consistency is used for the hand pressing of terra cotta in plaster molds or for soft-mud brick in wooden molds.

4. Fluid-clay bodies or "casting slips" in which the water content is sufficient to permit pouring into plaster molds are used for a number of pottery wares. Electrolytes are used to control the viscosity of the slip.

Atterberg[1] classifies the condition of a clay with varying amounts of water into five states, as follows: (1) the upper limit of fluidity or the point where the clay slip flows as water; (2) the lower limit of fluidity or flow where two portions of the clay mass can be made barely to flow together when placed in a shallow dish, which is sharply rapped with the hand; (3) the normal consistency or sticky limit, being the condition in which the clay is most workable, is no longer sticky and will not adhere to metal; (4) the rolling limit, or the condition in which the clay can no longer be rolled into so-called threads between the hand and the surface on which it may rest (this is the lower limit of the workable condition); (5) the condition in which the damp clay will no longer hold together when subjected to pressure.

Only two of these conditions are used to determine the plasticity number, the flow limit, and the rolling limit, which define the workable boundaries:

[1] KINNISON, C. S.: "A Study of the Atterberg Plasticity Method," *U. S. Bur. Standards, Tech. Paper* 46, 3. (1925).

The Flow Limit or the Upper Boundary of the Plastic Condition.[1]—About 5 grams of the clay powder of approximately 120 mesh are put into a small, porcelain evaporating dish and made into a paste by the addition of distilled water. By means of a polished-nickel spatula the mass is shaped into a smooth layer a trifle less than 1 centimeter in thickness. The clay is then divided into two portions by cutting a triangular-shaped channel through the mass, the lower edges being separated a trifle.

The dish is then sharply rapped 25 times against the heel of the hand in order to bring about the flowing together of the separated portions. The flow limit has been reached when the two portions of the clay can barely be made to meet at the bottom. If the paste is too thick or thin, water or clay is added until the proper consistency has been attained. The water content of the clay mass in this condition is then carefully determined by drying to constant weight, and the value is expressed in terms of percentage of the dry weight of the clay.

The Lower Plasticity Limit or the So-called Rolling Limit.—Clay in the stiff plastic condition is rolled between the hands, and any smooth surface is covered with paper until slender, cylindrical threads form. These "threads" may break up into smaller lengths, but this is of no significance. Dry clay powder is added to the plastic mass and thoroughly incorporated in it, and the rolling operation is repeated. The desired consistency has been attained when the clay can no longer be fashioned into threads by this method, but crumbles instead. This condition can be recognized without difficulty. The water is determined for this consistency and expressed in terms of percentage of the dry weight of the clay.[1]

Plasticity Number—The difference between the water contents of the flow limit and the rolling limit gives the Atterberg plasticity number. The higher its value, the more plastic the clay. It expresses the range in water content which a clay may have and still be considered plastic. Two clays may have the same plasticity number and yet their water contents for best plasticity may be widely different. It does not put the proper distinction between the plasticity of clays which are workable in the stiff-mud machinery and the sticky varieties which require a large amount of water to develop plasticity, but which are sticky instead of plastic and often have poor bonding power. From 20 clays studied by Kinnison, those clays

[1] *Loc. cit.*

are safely workable in the unmixed state of which the water of plasticity does not exceed 30 per cent and plasticity number of which is not more than 25.

Undoubtedly, simpler and just as accurate end points can be used instead of those of Atterberg. For instance, the lower limit could be that used in the dry-press process for floor tile, where the water content is such that the damp clay particles just hold together when squeezed in the hand. For the upper limit some common viscosity value used in casting slips for pottery would be suitable, with or without suitable deflocculents.

Water Adsorption. *Hygroscopic Water.*—G. Keppler[1] found the following percentages of water were adsorbed by various clays when kept over a 10 per cent sulphuric acid solution. The plasticity increases with the increase in hygroscopic water.

TABLE XX

	Per cent hygroscopic water	Pouillet effect, calories per 100 grams
Hirschau clay	3.02	79.6
Zettlitz kaolin	5.88	99.1
Lautersheim	7.51	174.7
Wildstein	8.00	183.0
Lothian	9.03	191.9
Fine Lothian	9.52	276.4
Ebernhahn	11.56	305.9
Fine quartz	0.70	14.7
Coarse quartz	0.40	
Zettlitz kaolin		
Calcined at 1400°	.....	28.0

The fine quartz is the elutriated product corresponding to "clay substance" in size. The coarse quartz contains 80 per cent fine quartz.

[1] KEPPLER, G.: "Berichte der Technisch-wissen shaftlichen absteilung des Verbandes keramischer Gewerke in Deutschland," p. 18 (1913).

Viscosity of Clay Suspensions(10).[1]—The coefficient of viscosity of a substance is closely analogous to the coefficient of internal friction.

The coefficient of viscosity of a fluid is the tangential force on a unit of area of either of two horizontal planes at the unit distance apart, one of which is fixed while the other moves with the unit velocity, the space between them being filled with the viscous material.[2]

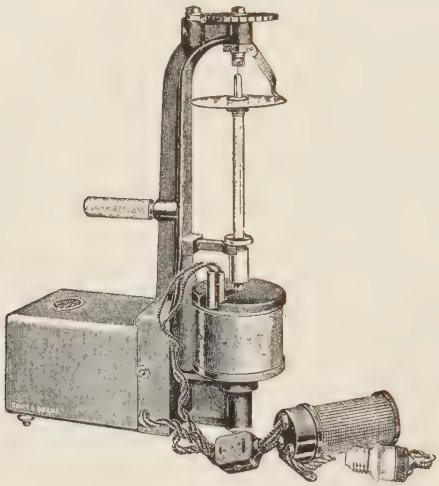


FIG. 14*A*.—The MacMichael viscosimeter. (*Eimer and Amend.*)

The systems which have been used to measure the viscosity of clay slips are of two general types: (1) the determination of the time required for a given volume of the slip to flow through a given orifice and (2) the measurement of the force required to move a given area through the slip at a given rate.

a. The Flow Viscosimeter.—Here the time required for a given volume of slip to pass a given orifice is noted. The Marriott principle of constant head(8)(10) or a varying head may be used(9).

[1] See reference No. 10, page 118.

[2] DUFF, A. W.: "A Textbook of Physics," p. 138, P. Blakiston's Son and Company, Philadelphia, 1909.

b. Torsion Methods.—The vibration of a heavy disk suspended by a wire in the slip may be determined(4) or a cup of the slip may be rotated at constant speed around the wire-suspended disk and the angular displacement noted(1) (Fig. 14*A*).

c. Rotation of a Paddle Wheel(5).—A paddle wheel is revolved by a given force, and the time required for a given number of revolutions is determined.

d. Measurement of the Force of Internal Friction(6)(7).—A hollow, cylindrical paddle immersed in the slip is rotated without mechanical connection by an associated revolving electromagnet. The current required to maintain a definite ratio of speeds between the magnet and paddle is the force used to determine the internal friction of the slip.

In these four methods, comparisons are made with the action of water under the same conditions of experiment. In order to derive some value for the plasticity of the clay, the amount of water required to bring the viscosity to some given value is taken as the direct numerical relationship for comparison with other clays. The fluidity, that is, the reciprocal of the viscosity, will be inversely proportional to the plasticity with equal concentrations of clay.[1] Some experimenters have used pure water or the clay in its original condition, while others have added electrolytes to flocculate or disperse the particles. The method of preparation, whether ball-mill grinding, blunging by agitation alone, the time of preparation and time of standing after dispersion, and the amount of air occluded, will all cause considerable variations in the viscosity. R. F. MacMichael-(1) used a standard viscosity equal to ten times that of water at 20° C., blunged the clay in a soda-fountain agitator, and flocculated the slip to its maximum viscosity with acid. The amount of water required to bring the viscosity to the standard was taken as the plasticity value.

Simonis(2) used a surface-tension value closely associated with viscosity. He determined the amount of water per

[1] Bleininger, A. V.: "Ceramic Processes Associated with Colloid Phenomena," *J. Ind. Eng. Chem.*, **12** (5), 437 (1920).

unit weight of dry clay which would give a standard resistance in pulling a small plate of glass from the surface of the slip.

References on Viscosity

1. MacMichael, R. F.: "Testing of Clay," *Trans. Am. Ceram. Soc.*, **17,** 639 (1915).
2. Simonis: *Sprechsaal,* No. 38, 597, 881, 1625 (1905); No. 39, 1167, 1184 (1906).
3. Elder, R. B.: "Interfacial Tension Measurements," *Idaho Bur. Mines and Geology, Pamphlet* 1.
4. Bleininger, A. V.: "The Viscosity of Clay Slips (Coulomb Viscosimeter)," *Trans. Am. Ceram. Soc.*, **10,** 389 (1908).
5. Bleininger, A. V., and G. H. Brown: "Note on Viscosity of Clay Slips (Stormer Viscosimeter)," *Trans. Am. Ceram. Soc.*, **11,** 596 (1909).
6. Bleininger, A. V., and H. H. Clark: "Viscosity of Clay Slips (Clark Apparatus)," *Trans. Am. Ceram. Soc.*, **12,** 383 (1910).
7. Emley, W. E. "The Clark Viscosimeter," *Trans. Am. Ceram. Soc.*, **15,** 401 (1913).
8. Schurecht, H. G.: "The Relation of Salt in the Purification of Clay (Mariott Tube Flow Viscosimeter)," *Trans. Am. Ceram. Soc.*, **19,** 468 (1917).
9. Shaw, J. B.: "American Clays for Floating Enamels (Shaw Flow Viscosimeter)," *Trans. Am. Ceram. Soc.*, **19,** 348 (1917).
10. Bleininger, A. V., and R. Horning: "Notes on Casting (Flow Viscosimeter)," *Trans. Am. Ceram. Soc.*, **17,** 330 (1915).
11. Kirkpatrick, F. A.: "Fitting Enamels to Plastic Clay Bodies," *Trans. Am. Ceram. Soc.*, **18,** 141 (1916).

Measurement of Colloid Matter(11). *Malachite-green Test for Gaging the Colloid Content.*[1]—Procedure:

Into a 100-cubic centimeter cylinder provided with a glass or rubber stopper put 50 cubic centimeters of water. Add 1 gram of clay, ground to pass a 60-mesh sieve. Shake at once by hand to prevent clotting. Add 50 cubic centimeters of malachite-green solution (6 grams malachite-green oxalate per liter). Shake gently for 2 hours on a mechanical shaker and allow to settle overnight. On the following day take out a convenient amount of the supernatant liquid by a pipette, the top of which is inserted to the 60-cubic centimeter mark of the cylinder, and run it into one of a pair of 50-cubic centimeter comparison tubes, such as used for carbon determinations in steel analysis. Into the other tube put 0.5 cubic centimeter of the standard dye solution (6 grams per liter) and dilute to about 35 cubic centimeters, the maximum concentration at which a good comparison can be made. Compare the tints in a camera with white glass plate. Now dilute whichever tube is the darker until the tubes match.

[1] Ashley, H. E.: "Control of Colloid Matter of Clays," *U. S. Bur. Standards, Tech. Paper,* 23, 40 (1911).

Calculate the total amount of dye adsorbed. This gives a value which is used in comparison with the amount of dye adsorbed by some clay chosen as a standard.

While the plasticity of clays is dependent on the amount of colloidal matter present, yet it is not certain that the colloidal matter in all clays has the same absorptive power for the green dye, nor that associated salts will not affect the results. The dark ball clays contain large quantities of organic colloids which must differ from the colloidal content of the primary kaolins which have not come in contact with organic materials.[1] This test measures the absorptive power of the colloids present and not the colloid content.

[1] MELLOR, J. W.: *Trans. Eng. Ceram. Soc.*, **21**, 96–97 (1921–1922).

CHAPTER V

DRYING CLAY

A. GENERAL THEORY OF DRYING

1. Vapor Pressure and Evaporation

The molecules of a liquid are in a state of vibration, the intensity of which varies with the temperature. At the surface some of the vibrating molecules are flying off as vapor molecules. If the surface of the liquid is enclosed, a vapor pressure will be built up in the enclosure until a certain maximum is reached which is constant at each given temperature. This means that the number of molecules passing from the liquid is equal to the number passing into the liquid. The vapor pressure of the liquid varies directly with the temperature and the rate of evaporation varies directly with the difference between the vapor pressure in the surrounding atmosphere and that of the liquid, or

$$\frac{dw}{dt} = (vp_1 - vp)K,$$

where $\frac{dw}{dt}$ = the rate of evaporation.

vp_1 = the vapor pressure of the liquid.

vp = the vapor pressure in the air.

K = the constant for the material.

A hygroscopic material, therefore, if placed in an atmosphere of constant humidity, will come to an equilibrium weight, gaining or losing moisture according to the relation between its initial vapor pressure and that of the atmosphere.

2. Temperature and Evaporation

The passage of the molecules from the surface of a liquid removes energy in the form of heat from the liquid, thus lowering the temperature. The vapor pressure of the

liquid will be lowered in this manner below the vapor pressure in the surrounding atmosphere, and evaporation will cease unless heat is supplied to the system. A source of heat, a means of supplying it to the ware, together with a means of removing the vapor which has emerged from the ware, are therefore essential for continuous evaporation.

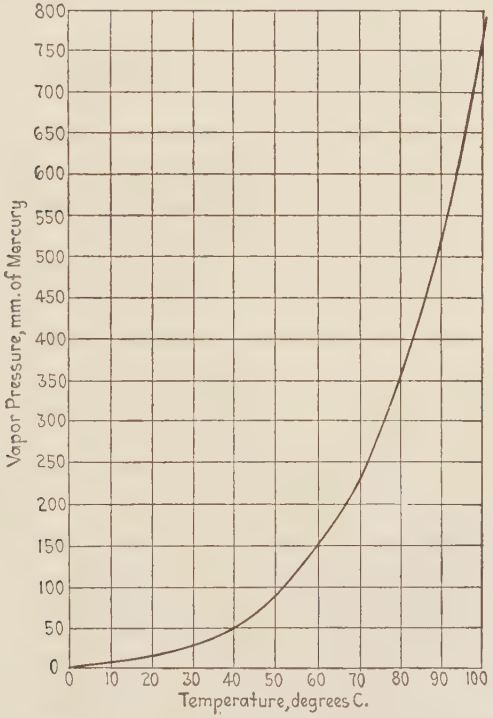


FIG. 15.—Vapor pressures at different temperatures for saturated conditions. (*Data from Landolt and Bornstein.*)

The lowering of the temperature of the liquid by evaporation is used to determine the evaporation "potential" by the familiar wet- and dry-bulb thermometer. The difference between the wet-bulb temperature and that of the temperature not influenced by this evaporation (dry-bulb temperature) is an approximate measurement of this potential or evaporation head. The depression of the wet-bulb temperature is also practically constant for any relative humidity for different dry-bulb temperatures.[1]

[1] Reference (5) at end of Chap. V, p. 136.

3. Relation between Air and Evaporation

Air is not necessary for evaporation but provides the most convenient method of supplying heat to the system, sweeping away the vapor, and thus producing continuous

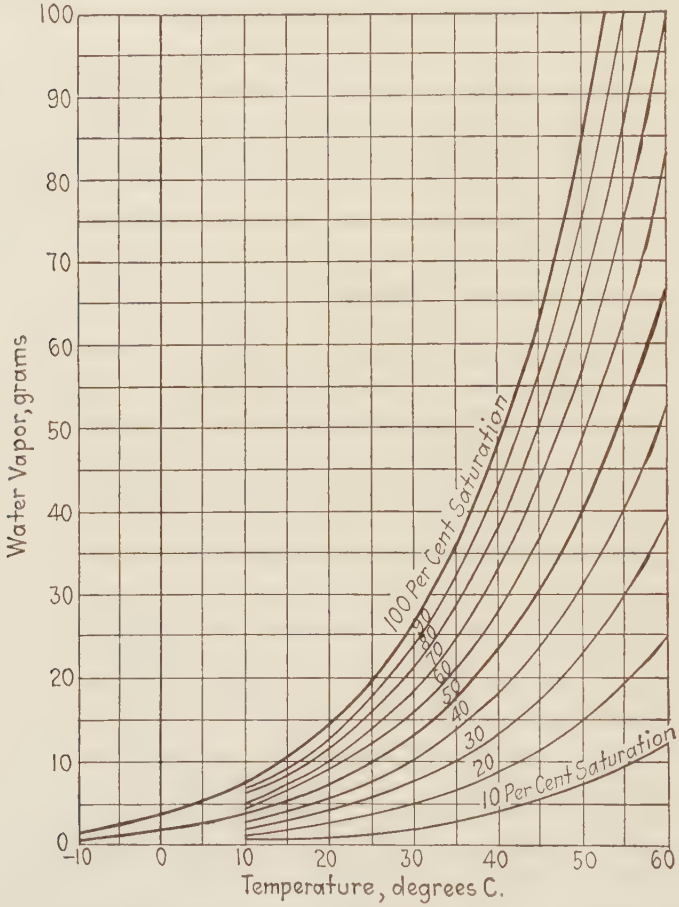


Fig. 16.—Grams of water vapor per kilogram of dry air. (*Landolt and Bornstein tables.*)

evaporation. After the moisture has been brought to the surface of clay ware and evaporated from that surface, it must be brushed away by moving currents of air to maintain a maximum rate of drying, for the normal rate of vapor diffusion from the saturated atmosphere surrounding

the wet clay into a quiet atmosphere is low. With a constant supply of heat to a free liquid surface, the rate of evaporation varies almost directly as the velocity of the air when the velocities are above 300 feet per minute(5). An imperfect diffusion of the vapor from the surface takes place below a velocity of 300 feet per minute. Also the evaporation increases approximately at a constant rate for every 230 feet increase in velocity(5). The direction of the flow of air with respect to the liquid surface is also

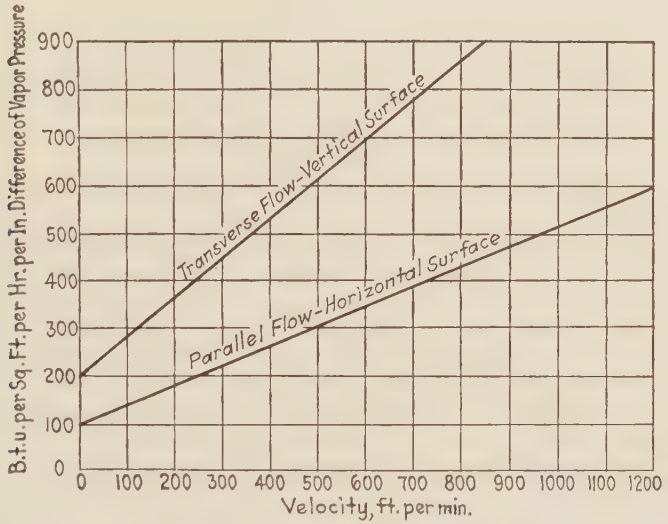


FIG. 17.—Heat transmitted by evaporation from a free-water surface and the effect of direction and velocity of the air currents. (*Stacey, Jr., A. E.: J. Am. Ceram. Soc.*, **8**, 459 (1925).)

important. The rate of evaporation when the air strikes the surface of the liquid perpendicularly is approximately double the rate when the flow is parallel to the surface(5) (Figs. 15, 16, and 17).

B. THE EVAPORATION OF WATER FROM PLASTIC CLAY

1. Composition of Plastic Clay

Plastic clay, suitable for commercial work is composed of three primary parts: (1) the cementitious, lubricating, colloidal clay portion which provides the plastic strength

and shrinks with drying and loss of water; (2) the non-plastic, non-lubricating portions, consisting of mineral sand, hard shale grains, artificial grog or feldspar, and flint of whiteware bodies, necessary to dilute or "open up" the plastic portion and prevent excessive shrinkage, warping, and cracking; and (3) the water films which are held onto the surfaces of all the particles and which assist in binding them into a yielding, moldable mass with sufficient strength to hold its own weight after shaping.[1]

Accessory portions of the plastic mass include: (1) various salts in solution, some of which are free to move to the surface in drying while a remaining portion is held by adsorption to the surface of the particles, and (2) pockets, bubbles or films of air, and dissolved gases.

2. Diffusion of Moisture through Clay

An intercommunicating but irregular system of capillaries of varying diameter is thus found in a mass of plastic clay(1).[2] As soon as the clay-water system is placed in an atmosphere whose water vapor is not saturated, the water from the clay surface will evaporate and will be replaced by capillarity from the interior. The rate of movement of water through the mass will depend on: the amount of water in the clay, the size and the changing diameter of the capillaries, and the character of the clay.

An excess of water in the clay will mean a high initial rate of evaporation equal to the rate from a free surface of water. It has been estimated that the resistance to the flow of water is inversely proportional to the fourth power of the diameter of the capillary channels(1).[2] While the initial rate of evaporation is similar for all clays, the character of the clay will soon make a difference in the rate of flow to the surface. The highly colloidal materials with their enormous surface area and fine capillary system will hold

[1] If the water content is so increased that the films exceed capillary or attractive dimensions and the particles are separated from each other beyond the range of molecular attraction, the yield value is lowered beyond the point where the body is able to hold its own weight.

[2] Reference (1), page 136.

onto the water more strongly than the open porous and sandy types of clay. Sodium chloride will slow up the evaporation of water from a clay. When the humidity of the surrounding atmosphere is high and the drying necessarily slow, the rate of evaporation approximates that of a free liquid surface. With low surrounding humidities, the rate of diffusion to the surface is usually much lower than the evaporation from an open liquid surface. Therefore, the rate of diffusion of moisture is a function of the temperature, it is dependent on the character of the clay, and a maximum rate can be found for each temperature. An increase in the velocity of air moving over the surface will not be able appreciably to increase the rate of drying over that of the maximum rate of diffusion.

3. Influence of Shape and Size of Clay Wares

Lindsay and Wadleigh(7)[1] found that with other conditions being equal, the rate of evaporation in per cent of clay weight varies as the area exposed to the air per unit weight of clay regardless of size and shape, with the understanding that all of the surfaces of a complicated shape are swept equally by air currents.

4. The First or Shrinkage Period of Drying

The water which is removed during the period of contraction is called "shrinkage water." It is equal to the volume lost during the drying period or the difference between the plastic and dry volumes. As drying progresses, the capillary films decrease in thickness, the grains are drawn by surface tension into close contact, and the mass as a whole is reduced in volume. This continues until a sufficient number of the particles are in contact to cause the total volume to remain constant(3).[1]

Free Liquid Rate of Evaporation.—During the initial portion of the shrinking period, when the water content is a maximum, the rate of evaporation is the same as that from a free water surface. The rate gradually decreases

[1] Reference (7) page 136.

as the free water is removed and the colloidal clay matter is able to hold onto its moisture more strongly. The change from the rate of free surface drying to that of restricted drying is not necessarily coincident with the point of final removal of the shrinkage water. The two will be closer with the open porous and more weakly plastic clays of low shrinkage water and farther apart in the highly colloidal clays having high shrinkage water and low pore water.

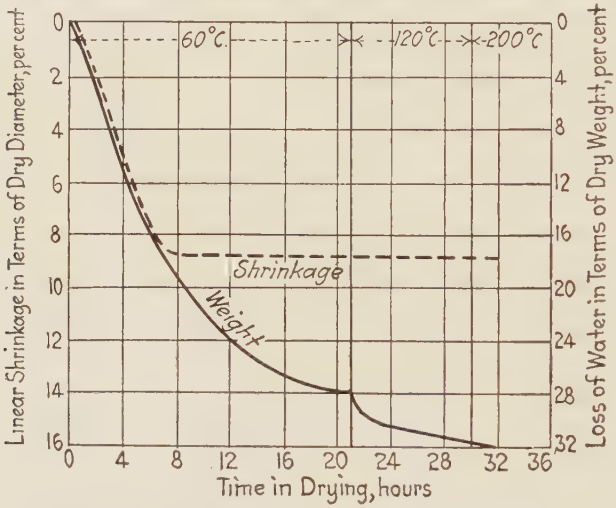


FIG. 18.—Drying curves of an Illinois glacial clay. (*Lines, E. F.: "Note on Drying of Clays," Trans. Am. Ceram. Soc.*, **10**, 146 (1908).)

Rate of Drying and Amount of Shrinkage.—Several writers have stated that the amount of shrinkage has been found to vary inversely with the rate of drying(1).[1] R. F. Geller(11)[1] found that the amount of shrinkage is not influenced by the rapidity of drying but is only proportional to the water content.

5. SECOND OR PORE-WATER PERIOD OF DRYING[2]

Pore water is that which remains in the clay after the shrinkage water has been removed. It is the difference

[1] See reference, p. 136.

[2] Some western United States clays have excessive pore space from volcanic ash, diatomaceous earth, etc. The fired shrinkage is therefore large if these materials are carried to vitrification.

between the total water of plasticity and the shrinkage water. After the volume contraction has ceased, a large number of the capillaries have been broken and the rate of diffusion becomes very slow. The larger grains of sand and grog which form the non-plastic skeleton are now in contact, but local shrinkage of the still wet, colloidal clay matter between the large grains can still proceed. The cessation of contraction is not abrupt, as the very definite amounts of shrinkage and pore water indicate, and is not uniform over a large piece of clay ware. The interior of a piece of grogged terra cotta may still be in the plastic condition while the edges and corners are gray hard. Warpage is an evidence of irregular diffusion and shrinkage.

Low Vapor Pressures.—With the capillary films broken, the final traces of water can be removed only as vapor and undoubtedly the vapor tension of the water films adsorbed to the clay particles has been lowered and high temperatures are necessary to remove the last portion. Lindsay and Wadleigh(7) found that the vapor pressure of the water left in the clay mass does not even approximate the vapor pressure of free water at the same temperature.

Hygroscopic Water.—According to the nature of the clay, the amount of colloidal material, and its structure, more or less mechanical moisture will be found in air-dried clay or in clay which has been dried to a higher temperature and then exposed to open-air conditions. Most of this is removed at 110° C., but in some cases higher temperatures are necessary.

6. The Temperature of a Clay Mass while Drying

The surface temperature of wet clay is similar to that of the wet-bulb thermometer during the initial period of drying or when the water supply is plentiful. The interior temperature of the clay is dependent on heat conductivity of the wet mass and the rate of moisture diffusion. The interior temperature can be made equal to the higher temperature of the surrounding atmosphere by increasing the vapor pressure of the surrounding air to saturation and

holding these conditions until the heat has penetrated the mass by thermal conduction through water and clay.[1] But just as a wet-bulb thermometer will increase in temperature until it reaches the dry-bulb temperature, if its water supply is cut off, so will the temperature of the clay mass gradually approach that of the air temperature when its water has been reduced to a very small amount or when the vapor pressure of the clay moisture is equal to that of the air moisture(7).[2]

As soon as the condition of free liquid evaporation ceases in the clay-water system, the comparisons between the wet-bulb thermometer temperatures and the wet clay temperatures fail, because of the lowering of the clay-moisture vapor pressure below that of water at the same temperature. The evaporation of water from the wet cloth surrounding the wet-bulb thermometer is approximately that of a free liquid surface. This means that the temperature of the interior of the clay must be raised above that of the wet-bulb temperature of the surrounding atmosphere to get a higher vapor pressure for the clay moisture so that drying may proceed. The clay temperature must be above the dew point or condensation temperature.

7. Drying Troubles

Strains.—Indications of strain in apparently uninjured pieces, are shown (but not proved) by variations in the dry strength and weaknesses developed during the early firing periods. This condition may be caused, however, by minute cracks which often close very tightly in the final drying period and escape observation. Strain is produced by variations in the amount of shrinkage, by irregular composition or water content, and by differential removal of the water.

[1] A steam or electrically heated metal die tends to produce case hardening of the surface if the interior of the plastic clay mass is not heated at the same time. If the steam comes in contact with the clay, however, it condenses and softens the surface. Friction generated in the auger machine also heats the clay, but the effect is often lost because of the delay in placing in the dryer. Noticeable stiffening does take place.

[2] See reference at end of Chap. V, p. 136.

Warping.—Change of shape during drying is caused (1) by the adjustment of the slower drying, plastic parts to meet the shrinkage of the stronger and faster drying portions until the mass is too rigid to bend back to its original shape; and (2) by irregular pressures used in molding or shaping thin ware. Water may be removed from one side of a piece of clay ware faster than from another by a freer circulation of air on the former side or because of the adsorption of water by a plaster mold or wooden pallet in contact with that side. Sagging from pressures or weights which exceed the yield value of the clay will cause a change of shape, but warping may take place in opposition to the force of gravity.

Checking and Cracking.—Clay in the plastic condition can be deformed without cracking. This property is gradually lost as the water is removed, the mass becomes more brittle, and the elastic limit may be exceeded by warping, sagging, or unequal shrinkage stresses. Checks are small surface cracks, which indicate a different set of conditions between the surface and the interior of many bodies, such as glazed bodies (crazing), cement floors, or painted surfaces. The surface cracks are caused by the higher or earlier shrinkage of the surface. The fine-grained, highly colloidal clays containing a minimum of non-plastic material and a maximum of water are the most difficult to dry without cracking. The finer the grain size, the smaller is the average capillary. Capillarity will thus be unable in many cases to maintain a sufficient supply of water in the outer surface to replace that lost by evaporation and to maintain a uniform water content between surface and interior. Shrinkage of the outer skin thus clogs the system until the condensation over the unshrunk interior has exceeded the tensile strength of the surface layer. Cracks perpendicular to the original surface appear and drying proceeds from the new surfaces of the cracks which continue to penetrate the mass.

Checking may also be produced by an unbalanced condition of the non-plastic content of a grogged body. Checks

will appear between large grog grains when too great a percentage of the large sizes have been used in proportion to the smaller non-plastic grains.

Checking may be produced by "finishing" or smoothing the surface of ware after it has dried beyond the plastic stage. This is true with grogged bodies finished with a stiff tool which drags those grog particles adjacent to the surface and produces small tears or checks which cannot heal again. Larger cracks are formed from a variety of manufacturing causes. (1) Vertical cracks will appear when the weight of large pieces of ware, together with the friction against the supporting surface, is too great for the tensile strength to pull the semiplastic mass together as it shrinks. The tensile strength is the weakest at the time of greatest contraction. On the other hand, at the period of lowest strength, it still retains the ability to stretch or deform under force. It is therefore commonly found that the per cent shrinkage of a large clay mass is greater in the vertical plane than in the horizontal. Drying boards are covered with sand or grog to prevent sticking and to reduce the friction. They are often tilted in order to obtain the assistance of gravity in pulling the mass of clay together. (2) Irregular shapes, especially those with small connecting areas, will often contract towards two or more centers and cause a crack to open at the weak connecting section.

Effect of Occluded Air on the Drying of Clay(14)(15).— Air will be caught (1) in a mass of dry clay by water films entering the mass simultaneously from all sides during tempering, or (2) by the folding over of plastic layers on each other as they are churned in the pugmill. (3) Air is caught in blungers, which are operated at speeds which cause splashing of the clay slip. (4) The water grinding of clay bodies in ball mills fills them with air in a very finely divided condition. (5) Gas bubbles are also produced within a body by bacterial action.

It has been estimated that as high as 25 per cent air by volume is contained in some porcelain insulator bodies,

and at least one mechanical means has been devised to expel the air by vacuum treatment from a plastic electrical insulator body(12). Air can be removed from clay slips by subjecting them to a partial vacuum; this will eliminate the troublesome bubbles in pottery casting slips. Large bubbles can be broken by pouring a casting slip in a thin sheet down an inclined trough or over a flat paddle. Bodies containing more of the sticky, plastic clay matter like ball clay, will retain air bubbles more effectually than some of the weaker bodies. Air bubbles can be slowly wedged out of a plastic clay mass by careful hand wedging or by the wedging wheels in use in the European shops, which squeeze the clay in two dimensions without rupture. Air, however, can be worked into a clay body by unskilled handling as well as it can be removed by careful treatment. Slow-moving blungers which do not splash the slip will gradually remove bubbles. The use of alkalies to "thin" casting slips will often release a multitude of bubbles. While it is not definitely understood, the standing or ageing of both plastic clays and clay suspensions must assist in the removal of air bubbles or at least give a better distribution. A gas worked into a body will weaken the plasticity (13). Bubbles of air will not displace water films which are already in contact with the clay grains for most clay particles, unlike some substances like gum arabic, are readily wetted in the presence of air. But the air bubbles will block the capillary channels and form continuous areas of separation. During the molding of a piece of clay ware under the high pressures, such as those of an auger machine for brick or tile, steam presses for sewer pipe, jigger tools working against pottery molds, or even the hand pressure used in molding terra cotta, the air bubbles are flattened into irregularly curved surfaces which spread throughout the mass and form planes of weakness. When the pressure is removed, the ability of the air-separated surfaces to cohere again is lessened by the tendency of the air film to draw up into the circular shape. This weak spot may become a center for radiating cracks. Larger volumes of air close to

the surface may cause trouble by thermal expansion if the ware is suddenly exposed to high temperatures in a hot drier. The high pressure of auger or steam presses will force air toward the center of the column and into the lamination planes. This action may be one of the principal reasons why lamination cracking is so troublesome. Those clays which laminate the worst are the ones which are able to retain the most air.

NOTE. **Body Air Bubbles in Glazed Plastic Stoneware.**—Tight, plastic stoneware bodies containing air bubbles will give trouble with glaze cracks. The ware has been molded by pressing a thin layer of plastic clay against a porous plaster mold with a jigger tool. Air bubbles will be flattened in a plane perpendicular to the pressure, and this shape will be retained by those bubbles next to the plaster surface by the quick absorption of water by the mold. By the time the piece is removed from the mold, the thin walls of clay between the air pocket and the surface will be strong enough to resist bulging. The inside of the piece may not show any cracking of this nature, because the jigger tool has broken and forced clay slip into all the air pockets near the surface in contact with the tool. The air in such flattened air pockets is not under pressure in the dry condition because of the porosity of the dry clay. Such ware is glazed in either the leather-hard or dry condition. Water from the glaze soaks the thin partition of clay on one side of the flat air space and gives the entrapped air an opportunity to bulge out and break through both the very wet clay and glaze layers. The flattened air space must lie very close to the surface for such a condition to develop. Porous, grogged bodies, such as those used in the manufacture of terra cotta, are not usually troubled with such surface cracks from air blebs,[1] because the air can more easily retreat into the more porous body behind as the water enters from the surface; the bubbles themselves are noticeably absent. A tight body dipped into a fluid glaze in the semidry or so-called leather-hard condition would probably give more trouble than a bone-dry body.

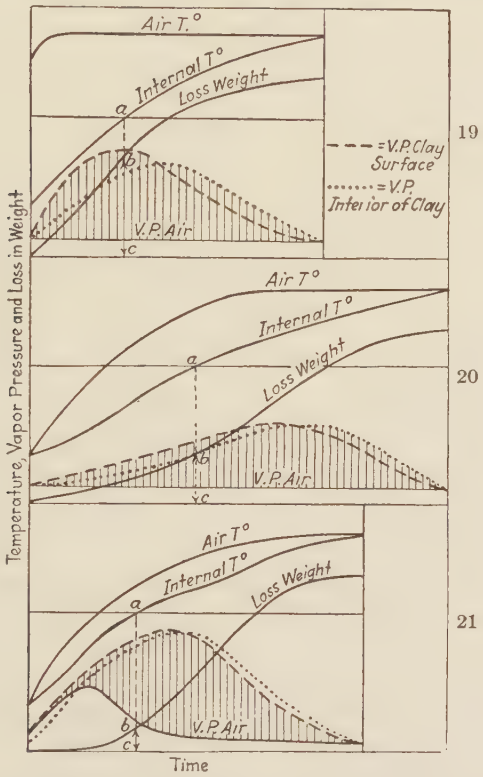
8. Commercial Drying

According to the temperature and humidity treatment, three types of drying systems with their modifications and combinations are found: (1) those in which the ware is subjected to a high temperature and low humidity throughout the whole drying period; (2) those in which the humidity remains low during the entire period, but the temperature is slowly raised; and (3) those in which

[1] WILSON, HEWITT: "Pinholing and Peeling in Terra Cotta," *Trans. Am. Ceram. Soc.*, **5**, 112 (1926).

the temperature is slowly raised but the humidity is kept comparatively high in the first part of the treatment and low in the second.

The first method is applicable to only fast-drying clays, for the shrinkage or cracking period is accelerated. The



FIGS. 19, 20, and 21.—The drying of a clay body under (19) low humidity and high temperatures from the start; (20) a more gradual increase in temperature and (21) humidity drying.

atmosphere surrounding the ware is such that the maximum diffusion of moisture to the surface and the maximum evaporation from the surface are attempted at all periods. In Fig. 19 an attempt is made to show the drying procedure in terms of vapor pressure. Fast drying from the surface starts immediately. The initial drop in temperature of the dryer due to the insertion of the ware is rapidly

recovered. A high-temperature differential between the interior and surface of the ware is shown by the rapid increase of the vapor pressure of the moisture at the surface and the slow increase at the center. In the later periods the vapor pressure of the interior may be greater than that of the surface because the water has been for the most part removed from the surface and not from the interior. Both vapor pressures have been lowered due to the adsorption and colloidal effects of the clay. The evaporation from the surface at the start of drying is similar to that from a free liquid surface and is increased due to the rapid rise in temperature of the surface alone. The critical temperature is passed without deference and after a large quantity of water has been removed. The period of stress is that preceding the critical temperature. The final loss of weight occurs when the vapor pressure of the interior moisture drops to that of the surrounding atmosphere and the interior temperature reaches that of the dryer. Case hardening and very irregular drying and shrinkage will take place with clays of slow moisture diffusion. This first method is a very rapid means of removing water, but it is not safe for most clays.

Figure 20 shows the second method or that usually employed for commercial drying. It is nothing more than the first method retarded during the period of stress so that the clay may accommodate itself to the shrinking and so that less differential in temperature and vapor pressure will be found between the surface and interior of the clay mass. This method is often supplemented by covering the ware with sacking during the period of stress to raise the vapor pressure of the atmosphere in contact with the clay surface and to retard this initial period more than shown in the sketch.

The third and more advanced method is shown in Fig. 21. An attempt is made to raise the temperature of the interior to the critical point before much evaporation has taken place and in this way to create a higher vapor pressure on the interior, not much lower than that of the surface

moisture. The temperature of the atmosphere is raised in a manner similar to that of the second method, but the per cent humidity and the vapor pressure of the atmosphere is immediately raised to a maximum just under the condition of condensation on the cold clay ware. The high surrounding humidity prevents evaporation until the interior temperature is raised above the critical point. The internal temperature has been following the rise in air temperature, but its rate of increase decreases after evaporation is under way. It may be probable that time is saved in heating the interior of a mass of plastic clay than in heating a partially dried mass, because of a possible greater conductivity of the tempering water. The difference between the temperatures and vapor pressures of the interior and surface clay is low throughout the entire period.[1]

The following factors must be studied for the most efficient drying conditions for each clay body, supplemented with variations for different shapes and sizes of ward:

1. Best rate of internal temperature rise.
2. Minimum or *critical internal temperature* from which drying can proceed at a rapid rate.
3. Maximum rate of drying after the critical internal temperature has been reached.
4. The cracking-slumping zone of humidity for various temperatures.

Up to the critical temperature the humidity must be kept high enough to prevent drying but must be below the condensation point to prevent slumping of the plastic mass. With some clays, a higher humidity can be carried at low temperatures than is possible at the higher temperatures. The best guide for regulating the condition in a dryer is the internal temperature of the clay body in conjunction with the wet-bulb thermometer and the loss-in-weight curve.

[1] Hot tempering water can be used to heat the interior of a clay mass, but in most cases, although some stiffening will take place in the open room, the bulk of the heat is lost because of the delay in placing the ware in the dryer for continued treatment. Some salts in the clay are likewise more soluble in hot water than in cold.

Application of Air Currents to Ware Surfaces.—The pieces of ware should be placed so that the air currents may circulate around them and strike the maximum surface area. Hollow terra cotta should be placed on edge whenever possible. Hollow block and tile should have circulation through the partition holes. One of the greatest difficulties in drying of solid brick has been the "hacking" of 500 or more brick in a fairly compact pile on a dryer car and trusting to natural circulation for air currents through the mass. The brick dryer of the future will have smaller units. The most important phase of the so-called "humidity" drying system outside of the control of the humidity has been the development of the rapid means of air circulation. The ejector system tempers the air by mixing that from the humidifier and heater with from three to five times its volume from the ware and thus prevents a sudden change of the air striking the nearest pieces of ware(6). Changes are therefore gradual and not abrupt.

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C. THE EFFECT OF PREHEATING ON THE DRYING PROPERTIES OF CLAY

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The plasticity, plastic working strength, water required for tempering, and drying shrinkage of most clays are decreased by preheating at comparatively low temperatures. This change becomes more marked with the increase of temperature. According to the nature of the clay, the change proceeds abruptly after reaching a certain temperature or is more or less gradual throughout. For most clays the best temperature range is between 200 and 300° C. The texture becomes more granular, the color darkens and, with ferruginous clays, assumes a reddish hue. The purer clays are affected more gradually by the heat treatment. The rate of drying of the preheated clays does not seem to differ from that of the unheated clays. Preheating offers a possible commercial method for the treatment of excessively plastic clays which cannot be worked and dried successfully by other means. The best minimum preheating temperature must be determined for each clay. Some

preheated clays seem to release their soluble salts more easily than the normal materials. Preheating apparently coagulates or agglomerates a portion of the colloids in the clay mass, analogous to the set of certain gels, gives a more granular appearance and feel, and a great porosity in the dried condition. In most cases the drying shrinkage is decreased at the expense of the burning shrinkage, which becomes greater than normal, and, if excessive, cracking may result. Such clays would not be benefited by this treatment.

Orton(3), working with the clays from the Great Plains, found the temperatures of 450 to 510° C. must be used and that it was necessary to practically eliminate the combined water and the hydrocarbons. The duration of the heat treatment was a critical matter, with apparently a margin of only 5 minutes in some cases. The commercial process involves the use of a suitable type of rotary kiln, a cheap fuel, a proper superintendence for control, and the cost of extra labor.

Lowenstein(5) found that clays lose some of their combined water at ordinary temperatures. This water may be restored by a slow resorption in a moist atmosphere. The plastic properties may thus be reduced to a minor extent as by preheating to higher temperatures. Sun drying after plowing aids the workability of soils and opens the structure.

D. THE EFFECT OF VARIOUS SALTS AND ELECTROLYTES ON THE DRYING PROPERTIES OF CLAY

In the drying process, the contraction in volume of the plastic clay is a typical property of colloid materials, which may give a shrinkage of 100 per cent of the true volume of the mass. The drying shrinkage is thus a measure of the colloidal content of the clay. The drying shrinkage will vary with the water used for tempering and the tendency to crack will vary with the amount of drying shrinkage and the ease of flow of water through the capillaries, or, in other words, with the amount of water to be removed and the uniformity of removal.

With most clays, the coagulating or flocculating salts, such as the chlorides and sulphates, increase the water content and the shrinkage. They may, however, as in the case of NaCl with many clays, tend to produce a more open structure with greater capillary flow and thus lessen the strain of water removal. Impure clays, with a system already loaded with adsorbed salts respond very differently to artificially added salts, and opposing data are found in the results of several investigators listed below.

Staley[1] and Bleininger[2] both found that sodium chloride decreased the cracking tendency of several troublesome clays. The drying shrinkage of Staley's sandy, loess clays from Iowa was increased, but the rate of drying was decreased by additions of common salt in amounts varying from 0.25 to 2 per cent of the weight of clay. He believed that the reduction of drying cracking was due to the production of a more porous structure, favoring better movement of the water through the capillaries. Any salt dissolved in water lowers its vapor pressure and the rate of evaporation. Salts that cause deflocculation of the colloidal clay particles tend to produce a structure which favors poor capillary action, with the result that the surface loses its water far ahead of the interior. Bleininger[2] found that the common salt greatly reduced the plasticity and drying shrinkage of very plastic clays. Soda ash decreased the rate of drying and increased the tendency to crack. Magnesium or calcium sulphate were harmful to the burning properties. Brown and Howat[3] added from 0.15 to 0.17 per cent caustic soda to various china and ball clays, bringing them to the point of maximum deflocculation, removed a small amount of impurities, and found that the drying shrinkage had been decreased a maximum of 1.05 per cent and that the burning shrinkage had been increased a maximum of 2.55 per cent. Back[4] found that the volume shrinkage of Georgia kaolin was increased by additions of NaCl up to 0.04 per cent and then was decreased about 1 per cent below normal when from 0.05 to 0.10 per cent salt was added. He believes that shrinkage increases with deflocculation and decreases with flocculation.

Addition of Lime.—Davis,[5] reasoning from the fact that lime is added to soils to improve their working conditions, added from 3 to 12 per cent

[1] Staley, H. F.: "The Effect of Salts on the Drying Behavior of Some Clays," *Trans. Am. Ceram. Soc.*, **17,** 697 (1915).

[2] Bleininger, A. V.: "The Effect of Electrolytes upon Clay in the Plastic State," *Eighth Intern. Cong. Appl. Chem.*, **5,** 24.

[3] Brown, G. H., and W. L. Howat: "The Use of Deflocculating Agents in the Washing of Clays and the Effect of the Process upon the Color," *Trans. Am. Ceram. Soc.*, **17,** 81 (1915).

[4] Back, Robert: "Effect of Some Electrolytes on Clays," *Trans. Am. Ceram. Soc.*, **16,** 520 (1914).

[5] Davis, N. B.: "Effect of Lime on Certain Cracking Clays," *Trans. Am. Ceram. Soc.*, **17,** 497 (1915).

hydrated lime to certain clays and stopped their cracking. He stated that some of the badly cracking clays must contain an excess of colloidal matter, such as high silicic acid or bentonite. These acids react with lime when intimately mixed and held in the moist condition, forming various lime silicates less active than the colloidal forms. The cost of the treatment would be prohibitive for cheaper wares. The addition of very much lime will likewise cause trouble in decreasing the vitrification range in firing.

E. DRY STRENGTH OF CLAY

The molecular cohesion of clay particles when brought within the range of molecular attraction, without intervening films of air or liquids is the most probable explanation for the dry strength of clay. Silicic acid or other cementitious colloids will bind the coarser clay particles together, but the strength of these colloids is due to the same force of molecular attraction. Such intimate contact of clay particles can either be made by high pressure or by the usual method of removing the tempering water from between the grains by evaporation. The water films pull the particles into contact as they leave through the capillaries, and thus prevent air films from forming planes of separation. Dried, dry-press wares are usually weaker than the corresponding dried wares made by the plastic process. In most cases the pressure has not been sufficient or uniformily distributed throughout the mass to bring as many of the grains into intimate contact as they would be by the water films. And even by the best process, the pore space of a dried brick shows that the colloidal contact is at best a very imperfect one. The increased strength during firing is largely caused by a more perfect contact from chemical reactions. When water is again added to a mass of dry clay, the superior disruptive force of the water films causes slight separation of the grains, and while the cohesive strength is reduced considerably, it is not eliminated unless the water content is increased to beyond that of the plastic condition.[1]

Bancroft[2] states that it should be possible to fit two pieces of broken porcelain together and restore the original piece,

[1] MacMichael, R. F.: "The Physics of the Clay Molecule," *Trans. Am. Ceram. Soc.*, **17**, 616 (1915).

[2] Bancroft, W. D.: "Applied Colloid Chemistry, General Theory," p. 140, McGraw-Hill Book Company, Inc. (1921).

but that the film of condensed air on the surface of the break prevents this coalescence. If the breaking and attaching were done in an absolute vacuum, the piece should theoretically be as good as new, but no one has produced the absolute vacuum. The principal in all cases is the intimate contact of clean surfaces. Highly polished copper surfaces will coalesce with a tensile strength of 98 grams per square centimeter. Glass surfaces can be ground and polished into optical contact, but nevertheless can be separated by sudden heating and cooling, by shearing forces, or by liquids which creep between the surfaces. This shows that the actual contact covers but a small percentage of the whole surface. Freshly split pieces of mica will coalesce by pressing them together, but a film of moisture, replaced in a few hours by a layer of grease, will prevent coalescence after exposure to air for 10 minutes.

Moisture Content and Dry Strength.—In the drying of most commercial wares, it is not important to remove the hygroscopic water and most wares are permitted to stand around the shop or in a cold kiln before firing. Yet to produce the maximum dry strength for laboratory testing it is very important to remove the last traces of moisture. In the standard procedure, drying is concluded at 110° C., and the test pieces are cooled in a desiccator to avoid the reabsorption of moisture.

CHAPTER VI

THE EFFECT OF HEAT ON CLAYS. VITRIFICATION

A. INTRODUCTION

From the chemical standpoint, dry clay consists of a large variety of silicates in various conditions and stages of combination. When clay is heated, some of the compounds are broken down, water vapor and other gases are evolved, while oxygen is taken into combination. Finally, when portions of the mass attain the fused condition, a new variety of complex alkali, calcium, magnesium, iron,

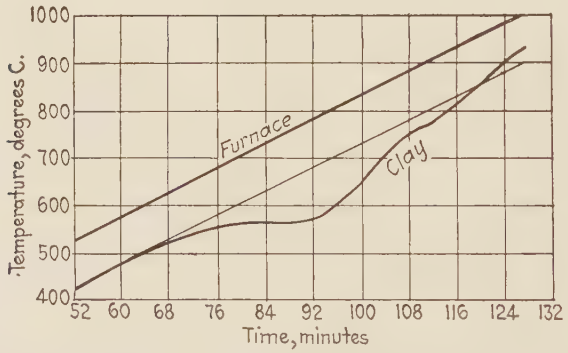


FIG. 22.—The heating curve of kaolin, indicating the endothermic and exothermic reactions. (*Brown and Montgomery, U. S. Bur. Stand., Tech. Paper* 21.)

and aluminum silicates are formed. The dehydration of the clay substance is an endothermic reaction (Fig. 22) and is associated with an increase in molecular volume. At about 900° C. an exothermic reaction occurs which is associated with the dissociation of the aluminum silicate into amorphous mullite and silica.

As the vitrification temperatures are reached, the external volume contracts, due to the effect of surface

tension of the fused portions. This continues until the pore space is practically closed, a condition which is called complete vitrification. While surface tension is the most important factor in causing a decrease in pore space, vaporization has some effect.[1] Many of our ceramic materials, whose vapor pressures have been commonly considered negligible, vaporize rather freely at higher temperatures. Iron oxide may be used for cream colors in glazes up to cone 4 or 5. At cone 6 or 7, however, it vaporizes slowly and gives unreliable and varying cream tones. Chromium oxide vaporizes freely in glaze kilns; zinc and barium oxides vaporize instead of melting under the usual oxidizing conditions; and the melting point of magnesia can be determined only in special atmospheres such as a mixture of carbon monoxide and nitrogen. In air and in vacuum, the magnesia vaporizes before the melting point can be obtained.[2] Lead oxide, boric acid, and the alkalies vaporize at comparatively low temperatures and both silica and alumina at high temperatures. In the electric furnace silica is reduced to the monoxide. Lime vaporizes very quickly at cone 41 (approximately 1970° C). Hence, as one portion of a piece of clay ware is heated to a temperature above that of another portion, vaporization and condensation will tend to fill the cooler pore spaces, distribute fluxes, and assist in vitrification and fusion.

The amount of pore space filled is not the same for different clay wares. Some products like fire brick, porous wall tile, etc. are fired to only a comparatively low degree of vitrification; others like paving brick or porcelains are carried to a very high degree.

[1] Bleininger, A. V.: "Ceramic Processes Associated with Colloid Phenomena," *J. Ind. Eng. Chem.*, **12**, No. 5, 438 (1920).

[2] Kanolt, C. W.: "Melting Point of Some Refractory Oxides," *U. S Bur. Standards, Sci. Paper* 212, 304 (1913).

B. CHEMICAL AND PHYSICAL CHANGES OF PURE KAOLIN WHEN HEATED

Temperature	Composition and Changes
20 to 150° C.	Mechanical and hygroscopic water are eliminated
400 to 600° C.	The two molecules of water in $Al_2O_32SiO_2$-$2H_2O$ are removed in an endothermic reaction accompanied by an expansion in specific volume[1] (Fig. 23)
850 to 1050° C.	An exothermic reaction occurs, resulting in the dissociation of the $Al_2O_32SiO_2$ to form amorphous mullite,[1] $3Al_2O_32SiO_2$ plus tridymite, SiO_2(13)(4)
1350° C. (plus or minus)	Beginnings of crystallization of mullite(4)
1470° C.	Tridymite is unstable above this temperature and cristobalite is the stable form of silica(14)
1545° C.	The eutectic, between cristobalite and mullite forms. It consists of 5.5 per cent alumina and 94.5 per cent silica(15)
1745 to 1790° C.	The final melting point of the original kaolin composition, $45.87Al_2O_3$ and $54.13SiO_2$(16)
2000° C. (plus or minus)	Reduction and vaporization of SiO_2 to SiO resulting in a closer approach of the remainder to pure mullite(17)

[1] Some of the English ceramists disagree with this idea. See references 2, 3, and 7.

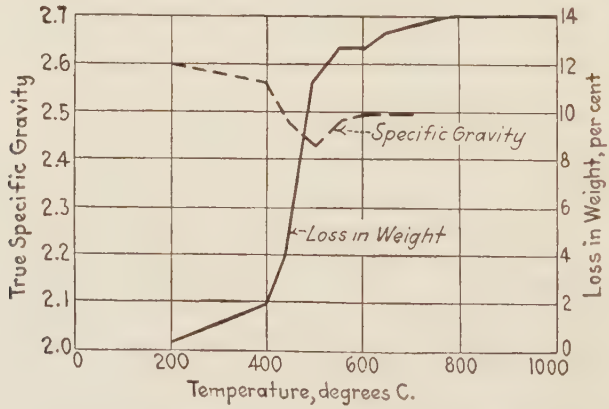


Fig. 23.—The loss in weight and change in specific gravity as a kaolin is heated to dehydration temperatures. (*Brown and Montgomery: U. S. Bur. Stand., Tech. Paper* 21.)

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17. Wilson, Hewitt, and C. E. Sims: "Artificial Sillimanite (Mullite) as a Refractory," *J. Am. Ceram. Soc.*, **7,** 842, 907 (1924).

C. THE DEHYDRATION-OXIDATION FIRING PERIOD

The firing of clay wares is ordinarily divided into three periods:

1. Dehydration
   - *a.* Mechanical dehydration or "water smoking," 20 to 150° C.
   - *b.* Chemical dehydration or "chemical water-smoking," 150 to 600° C.
2. Oxidation, 350 to 950° C.
3. Vitrification, 900° to plus, followed by fusion.

These periods vary with different types of clays and with the impurities present. It is apparent from the nature of the reactions, however, that the oxidation period overlaps both the dehydration and the vitrification periods (Fig. 24). Water and volatile matter will be removed and oxidation reactions will proceed within the temperature ranges given

above for all types of clays, but vitrification is dependent upon the type of clay and the fluxing impurities present. When the carbon content is large, the oxidation and elimination of sulphur and the oxidation of iron compounds will be retarded. Likewise, because of the CO_2 pressure in the

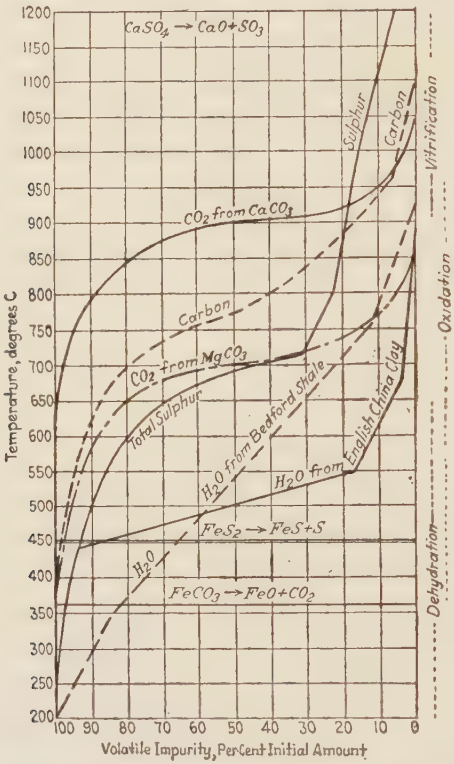


FIG. 24.—Approximate removal of volatile impurities from common clays when heated.

pore spaces, the dissociation of the calcium and magnesium carbonates will be delayed. Carbon has a stronger affinity for oxygen than sulphur, and sulphur a stronger affinity than ferrous oxide. Hence, it is imperative that both the carbon and sulphur be removed before the bright-red colors of ferric oxide can be produced.

The dehydration and oxidation periods have been combined because it is impossible to make a temperature divi-

sion which will separate the two classes of reactions. The dehydration period includes the expulsion of any mechanical water left in the ware from tempering which has not been removed during the drying process; hygroscopic water absorbed from the atmosphere; water from silicic acid and other colloids and that water combined chemically with the original silicate molecule and other accessory minerals. While the average rate of removal is greatest near 500°, the final traces may continue until near 800°. The water loss is a function of both time and temperature and may be accomplished at certain lower temperatures if the time is increased.

The oxidation period, which starts with the oxidation of the easily ignited organic matter and sulphur, near 350°, continues until the last traces of graphite or other forms of hard carbon are burned out. It thus overlaps the period in which water is lost and may be delayed until the surface of the ware has vitrified or sealed over. It is therefore advisable to use clays in which the volatile impurities are small in amount and are easily removed before vitrification develops.

The dehydration-oxidation period shows a reduction in weight and an increase in porosity with a small increase

TABLE XXI.—LOSS IN WEIGHT AT DEHYDRATION TEMPERATURE[1]

Type of clay	Initial loss, degrees Centigrade	Maximum rate, degrees Centigrade	Final loss, degrees Centigrade	Per cent loss in weight
Kaolin	400	500	800	10.9–14.5
Ball clay	400	500	700	11.2–18.2
High-grade flint fire clay	400	500	700	11.0–25.0
Common plastic fire clay	400	500	700	6.0–10.0
Shales	400	600	800	4.6–21.3
Surface clays	200	600	625	4.0– 8.0

[1] BROWN, G. H., and E. T. MONTGOMERY: "Dehydration of Clays," *U. S. Bur. Standards, Tech. Paper* 21, 1913.

KENNEDY, W. M.: "Relative Point Dehydration of Pure and Calcareous Clay," *Trans, Am. Ceram. Soc.*, **4**, 146 (1902).

in volume. During the vitrification period, the weight remains nearly constant, but both the porosity and volume diminish.

Kaolins, ball clays, and high-grade flint clays approximate the theoretical dehydration loss for kaolinite, 13.9 per cent. Dark-colored ball clays will sometimes have a large loss due to the oxidation and removal of large contents of carbonaceous matter. The more impure types of clay show the effect of dilution with non-hydrous minerals, but in some cases the presence of carbon, sulphur, and carbonates may raise the loss to above 20 per cent. The presence

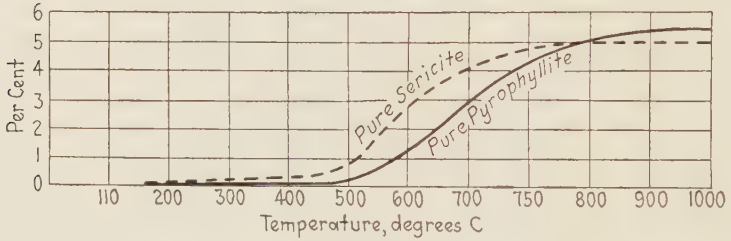


FIG. 25.—Dehydration of sericite, $K_2O3Al_2O_36SiO_22H_2O$ and pyrophyllite, $Al_2O_34SiO_21H_2O$. (*Stuckey, J. L.: J. Am. Ceram. Soc.*, **7**, 736 (1924).)

of halloysite with a chemical water content of 19.6 per cent also raises the dehydration loss. Figure 25 shows the dehydration of sericite and pyrophyllite.

2. Dehydration and Loss of Plasticity

Brown and Montgomery's experiments[1] showed that surface clays lose their plasticity at the lowest temperatures, near 400° C., followed in order by ball clays at 450° kaolin at 500 to 600°, No. 2 fire clays from 600 to 750°, and shales from 750 to 800°. No direct comparisons can be drawn between chemically combined water and plasticity, for dehydration does not necessarily destroy the plasticity of clays.

[1] Brown, G. H., and E. T. Montgomery: "Dehydration of Clays," *U. S. Bur. Standards, Tech. Paper* 21, 22 (1913).

3. Rehydration of Clay[1]

As in the case of the dissociation of kaolin, conflicting statements are found concerning the rehydration of clay. Laird and Geller[2] found that kaolin on dehydration forms an anhydride between 500 and 700°, which can be changed again to the hydrated condition by heating in water to temperatures of 200 to 270° for a sufficient length of time (8 to 48 hours). The rehydrated material was found to be, in general, plastic and appears colloidal, resembling raw clay,[3] Mellor and Holdcroft[4] were able to restore only from 3 to 4 per cent water by heating calcined kaolin (600 to 640°) under pressure in steam, and, as the material did not regain its plasticity, they concluded that this was the rehydration of alumina or silica and not kaolin.

4. Compounds of Iron with Sulphur(17)[5]

The three most common forms of oxidizable sulphur which occur in clays are: pyrite, marcasite, and pyrrhotite. The first two, FeS_2, are more common than the third, pyrrhotite, approximately $Fe_{11}S_{12}$, which can be removed by magnetic screening. Pyrite and marcasite become magnetic after heating to low temperatures and the removal of part of their sulphur. Marcasite decomposes more rapidly than does pyrite, both at atmospheric and advanced temperatures. Mellor(21) has found cupriferous pyrites in English clays, but they are not common in American clays. On weathering, these sulphides break down to iron sulphate.

Many coal-measure shales contain as much as 4 per cent bituminous matter and 2 per cent pyrite. The average periodic kiln will hold 100,000 face brick. The average

[1] See Chap. V, p. 137.

[2] Laird, J. S., and R. F. Geller: "The Rehydration of Calcined Clays," *J. Am. Ceram. Soc.*, **2**, 828 (1919).

[3] It may be possible to decompose feldspar in an autoclave to form a hydrated aluminum silicate.

[4] Mellor, J. W., and A. S. Holdcroft: "The Constitution of the Kaolinite Molecule," *Trans. Ceram. Soc. (England)*, **10**, 106 (1910–1911).

[5] See reference 17, p. 153.

weight per 1,000 brick is 3 tons. The kiln will then contain 12 tons of fuel or carbonaceous matter and over 3 tons of combustible sulphur.[1]

The Effect of Heat on the Iron Sulphide.—The decomposition of FeS_2 when slowly heated in a kiln usually proceeds with the formation first of FeS between 350 and 500° C., which in turn passes to the oxide or sulphate (500 to 800° C); or it is possible that the FeS_2 may pass directly into the sulphate (600 to 735°). A rapidly moving oxidizing atmosphere, even though the oxygen content be only 10 per cent, is sufficient to readily and almost completely decompose pyrite at low temperatures(22). If the gas products of the oxidation are not removed rapidly, they will combine with portions of the ware to form compounds which will not be decomposed until higher temperatures. The rate of gas flow is more important in this case than the rate of temperature increase(22). The formation of SO_2 or SO_3 will depend on the oxygen content of the surrounding combustion gases, the temperature, and the catalytic action of the heated clay ware. The equilibrium reaction is expressed as follows:

$$2S + 3O_2 \leftrightarrows 2SO_3 \qquad (1)$$

To FeS:

$$FeS_2 + O_2 = FeS + SO_2 \qquad (2)$$

$$2FeS_2 + 3O_2 = 2FeS + 2SO_3. \qquad (3)$$

The above reactions start slowly at 350° C. and go to completion at 425° if the temperature is held. In most cases they are complete below 505° under commercial conditions. Without sufficient oxygen, sulphur may be condensed in the cooler parts of the kiln. If the clay is subjected to strong reducing conditions between 400 and 500° C., hydrogen sulphide may be formed with the water of chemical combination which is being evolved at these temperatures.

$$H_2O + SO_2 + 3C = H_2S + 3CO \qquad (4)$$

[1] Stull, R. T., and Hursh: "Tests on Clay Materials in Illinois Coal Mines," *Illinois Geol. Survey Bull.* 18, 21 (1917).

Possible reactions in changing FeS to oxides and sulphates:

$$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2 \quad (5)$$
$$4FeS + 9O_2 = 2Fe_2O_3 + 4SO_3 \quad (6)$$
$$FeS + 2O_2 = FeSO_4 \quad (7)$$
$$2FeS + 5O_2 + SO_2 = Fe_2(SO_4)_3 \quad (8)$$

The above reactions normally start at about 500° C. and should be complete before 800° C.

It may be possible for *ferric sulphide* to pass directly into the *sulphate* forms as follows:

To ferric sulphate:

$$2FeS_2 + 7O_2 = Fe_2(SO_4)_3 + SO_2 \quad (9)$$
$$4FeS_2 + 15O_2 = 2Fe_2(SO_4)_3 + 2SO_3 \quad (10)$$

To ferrous sulphate:

$$FeS_2 + 3O_2 = FeSO_4 + SO_2(600 - 735° \text{ C.}) \quad (11)$$
$$2FeS_2 + 7O_2 = 2FeSO_4 + 2SO_3 \quad (12)$$

Iron sulphates may be dissolved during the chemical hydration period and spread over the surface, leaving a brown scum of oxide on buff-colored wares after the sulphate has been dissociated.

Decomposition of Iron Sulphates.—In the presence of an atmosphere of oxygen,

$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$ (between 560 and 775° C.) (1)

When oxygen is present any carbon will burn out first and leave the ferric sulphate to decompose later as above in Eq. (1). But if the oxygen supply is low, the ferric sulphate will be attacked by the carbon:

$$Fe_2(SO_4)_3 + 3C = Fe_2O_3 + 3CO + 3SO_2 \quad (2)$$

or

$$Fe_2(SO_4)_3 + 3CO = Fe_2O_3 + 3CO_2 + 3SO_2 \quad (3)$$

Ferrous sulphate gives a similar series of reactions:

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3 \text{ (oxidizing)} \quad (4)$$
$$FeSO_4 + C = FeO + CO + SO_2 \text{ (reducing)} \quad (5)$$
$$FeSO_4 + 2C = FeS + 2CO_2(735 - 775° \text{ C.}) \quad (6)$$

Absorption of Sulphur Oxide Gases by Clay Ware.—Sulphur dioxide and trioxide in the combustion gases are

absorbed by heated clay ware in the kiln until a temperature of about 760° C. is reached. The dioxide is dissolved in the surface moisture (or as H_2SO_3) up to 100° C. after which it is released. The trioxide is held by the surface moisture as H_2SO_4 up to 100° C. and during this time may attack the accessory basic minerals of lime, magnesia, alumina, alkali, and iron. The sulphuric acid is not decomposed until near 260° C. Ferric sulphate may be formed throughout the ware at temperatures up to 600° C. by the reaction of free ferric oxide in the clay with the sulphur oxide gases or solutions. Sulphur may also be confined in the clay in an insoluble form, sulpho-silicate or ferrous sulpho-silicate, at all temperatures up to 700° C.

Jackson(23) did not find that as much sulphur was absorbed by clays from kiln gases as was expected. Although even under extreme conditions only a small amount of the bases present was converted to sulphates, yet but a small amount is needed to produce efflorescence. The absorption of sulphur was more a function of temperature than of time of treatment, the amount of bases present in the clay or the per cent of sulphur in the coal. The temperature of maximum absorption was 495° C. Because only 1 per cent SO_2 can be developed in a kiln atmosphere by firing a 5 per cent sulphur coal in 100 per cent excess air, the dilution is too great to retard the evolution of sulphur gases from the sulphur compounds in the clay. Water vapor is the only intermediate factor needed for the attack on the bases in the clay by the sulphur gases. Therefore dry ware and a good draft during the water-smoking period are the best preventives against the formation of efflorescence from kiln gases.

Analytical Methods for Sulphur Determination in Clay(19).

Water-soluble Sulphur.—Sulphurous and sulphuric acids, some sulphides, sulphites, and sulphates. Boil 10-gram samples of the powdered clay in 500 cubic centimeters of distilled water and filter. Boil filtrate and add a little bromine water and a few drops of HCl. If still clear, add barium chloride solution to complete precipitation.

Remaining Pyrite.—The insoluble residue from the above procedure is treated with 50 cubic centimeters of concentrated HNO_3, 100 cubic centimeters of concentrated HCl, and 350 cubic centimeters of distilled water and again boiled for 30 minutes. This aqua regia changes the pyrite to ferric sulphate, and the sulphur content is determined as above after evaporating most of the excess acid.

Sulpho-silicate.—While this method has not been thoroughly developed, it is based on the extraction of the sulpho-silicate by a mixture of dilute nitric acid and hydrofluoric acid in a platinum dish on a steam bath. The nitric acid is used to oxidize any SO_2 to H_2SO_4 which is not vaporized at steam-bath temperatures.

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18. "III. The Behavior of Calcium Compounds in Clays," *J. Am. Ceram. Soc.*, **7,** 427 (1924).
19. "IV. The Absorption of Sulphur Gases by Ferric Oxide in Clay," *ibid.*, 532 (1924).

20. "V. A Quantitative Study of the Nature of Sulphur Evolution in Kiln Firing," Part I, *ibid.*, 634 (1924); Part II, 656 (1924).
21. Mellor, J. W.: "Collected Papers," **1**, 123 (1914).
22. Jackson, F. G.: "The Oxidation of Ceramic Wares during Firing, VI. A Laboratory Study of the Effect of Varying the Rate of Gas Flow and of Heating on the Decomposition of Pyrite in Clay," *J. Am. Ceram. Soc.*, **8**, 534 (1925).
23. Jackson, F. G.: "A Chemical Study of the Absorption of Sulphur Dioxide from Kiln Gases by Ceramic Ware," *J. Am. Ceram. Soc.*, **9**, 154 (1926).

5. The Dissociation of Calcium Carbonate

When heat is applied to calcium carbonate, carbon dioxide is liberated with the formation of calcium oxide:

$$CaCO_3 \rightleftarrows CaO + CO_2$$

If heated in a closed vessel to a constant temperature, all of the calcium carbonate is not dissociated and the three phases can exist in equilibrium together. The pressure of carbon dioxide gas has increased within the container until the reaction is stopped in a manner similar to the equilibrium established by the vapor pressure of water in a closed vessel. If the temperature is raised, more CO_2 will be liberated and a new adjustment will be made, because the system possesses but one degree of freedom or variability. This means that if either the temperature or pressure is changed, the system will adjust itself to equilibrium again[1] (see Chap. VII, p. 212).

If the heating takes place in the open air or kiln, the back pressure acting against the dissociation pressure consists of the small carbon dioxide pressure of the atmosphere (3 to 4 millimeters of mercury), the CO_2 content of the products of combustion in a fuel-fired kiln, or from the dissociation of limestone in a lime kiln. At ordinary temperatures and normal atmospheric conditions the partial pressure of CO_2 in the atmosphere is greater than the dissociation pressure of $CaCO_3$; hence, the carbonate is the stable form and quicklime reverts to $CaCO_3$ on standing. The dissociation pres-

[1] Findlay, A.: "The Phase Rule," 5th ed., pp. 2, 8, 12, Longmans, Green & Co., London (1923).

sure becomes equal to the partial pressure of carbon dioxide in the air near 600° C. At temperatures slightly above 600°, the dissociation occurs very slowly, it is true, but completely if the heating is done in the open air. At 898° C. the dissociation pressure equals the total atmospheric pressure of 760 millimeters of mercury. This temperature is therefore called the "dissociation temperature."[1] In the cement, lime, and clay industries, the impurities are said to lower the temperature of dissociation. Bleininger and Emley[2] found that 880° C. was the dissociation temperature of an impure limestone.

6. The Dissociation of Gypsum, $CaSO_4.2H_2O$

In a similar manner, gypsum will eventually lose all of its water if the temperature is held at 80° C., the water vapor is removed as fast as liberated, and the partial pressure of the water in the atmosphere is kept close to zero. The theoretical temperature required to reduce the water content to one-half a molecule of H_2O[3] (hemi-hydrate) is 107° C.

Calcium sulphate may be formed from calcium carbonate when in contact with sulphur gases in driers and kilns if water is present. A well-ventilated kiln containing dry ware will show less scum than one containing wet ware with poor draft.

When a clay which contains gypsum is heated in an oxidizing atmosphere, the sulphate, $CaSO_4$, does not show appreciable dissociation until 1210° C. The action is rapid at 1325° C.[4] These temperatures are above the best vitrification period for many red-firing clays and therefore may cause a form of high-temperature bloating or vesicular structure.

[1] Johnson, J.: *J. Am. Ceram. Soc.*, **32**, 8 (1010).

[2] Bleininger, A. V., and W. E. Emley: Discussion, *Trans. Am. Ceram. Soc.*, **18**, 884 (1916).

[3] "Gypsum Properties, Definitions, and Uses." *U. S. Bur. Standards, Circ.* 108 (1921).

[4] Bole, G. A., and F. G. Jackson: "The Oxidation of the Incidental Minerals Found in Clays," *J. Am. Ceram. Soc.*, **7**, 427 (1924).

Another method of getting rid of the sulphate is to provide a reducing atmosphere. Seger[1] states that sulphuric acid which has been taken up by the brick may be reduced and driven from the kiln as sulphurous acid. A. E. Williams[2] was able to reduce gypsum in an atmosphere of CO as low as 800° C., and Powell[3] found that $CaSO_4$ could be reduced to the sulphide at 500° under extreme reducing conditions, such as in the coking of coal. Bole and Jackson[4] also reduced gypsum in an atmosphere of natural gas between 700 and 850° in amounts of 15 to 95 per cent depending on the temperature. The products of the reaction consisted approximately of one-half calcium oxide and one-half of a mixture of sulphite and sulphide. For commercial work, the temperature of the bottom of the kiln should have reached 700°, and the reduction should not be severe enough to carry the reaction to the sulphide. Bole and Jackson recommend the following procedure:

$$CaSO_4 + CO = CaSO_3 + CO_2$$
$$CaSO_3 + \text{heat} = CaO + SO_2$$

followed by a reoxidation to restore as much of the red iron color as possible.[5]

D. THE VITRIFICATION PERIOD. 900° C. PLUS

1. Physical Changes during Vitrification

Introduction.—Vitrification is a partially fused condition of a fired piece of clay ware, in which the pore space is small and the exterior volume is near a minimum. The hardness is greater than that of steel, and the structure is in the period of greatest toughness and strength. Vitrifica-

[1] Seger, H.: "Collected Writings," **1,** 128.

[2] Williams, A. E.: "Dissociation of Calcium Sulphate," *Trans. Am. Ceram. Soc.*, **18,** 271 (1916).

[3] Powell: *J. Ind. Eng. Chem.*, 1069 (1920).

Hofman and Mastowitsch (*Trans. Inst. Am. Mining Eng.*, **39,** 628) state that $CaSO_4$ in contact with silica decomposes at 1000° and in contact with ferric oxide decomposes at 1100° C.

[4] *Loc. cit.*

[5] Jackson: *J. Am. Ceram. Soc.*, **7,** 427 (1924).

tion precedes deformation of shape which is due to the excess development of fused and glassy material or to the production of a vesicular structure due to the expansion of gas vesicles. The vitrification period covers a range of temperatures in which the pore space and exterior volume are usually diminishing, though they may in some cases remain practically constant. Professor Orton's legal definition of vitrification[1] for heavy clay products is based on open pore space alone and requires a water absorption not greater than 3 per cent of the dry weight of the sample. Electrical and fine porcelain must have an absorption less than 0.25 per cent.

During the dehydration-oxidation period the pore space has been enlarged by the expulsion of volatile matter. The exterior volume has likewise been increased due to the specific volume increase of the clay substance and, in the case of sandy clays, to the expansion of the quartz. Some shrinkage of the colloidal material occurs, however, before the shrinkage which is due to fusion. But most of the decrease in volume of common clays is caused by partial fusion of the clay mass, giving surface tension an opportunity to draw the fluid material through the capillaries. The temporary thermal expansion of the clay is overtaken by early fusion in low-burning red clays. While changes in specific gravity are of sufficient magnitude to increase the volume during the dehydration period, yet during the vitrification period, they are decidedly inferior to the contraction due to fusion. Vitrification is then dependent upon the amount and fluidity of the fused portion together with the amount and character of the pore space to be filled. The vitrification zone always lies below the deformation zone and is dependent upon the same factors.[2] The lower limit of the vitrification zone is fixed by the temperature at which the eutectic composition of the

[1] Orton, Jr., E.: "The Legal Definition of Vitrification," *Trans. Am. Ceram. Soc.*, **16**, 511 (1914).

[2] Staley, H. F.: "Melting Point and Deformation Point Eutectics," *Trans. Am. Ceram. Soc.*, **13**, 674 (1911).

components present begins to liquify. The greater the fluidity and the greater the quantity of the fused portion, the more narrow the vitrification zone. Feldspar is a "safer" flux than lime, because the high viscosity of the melted feldspar retards its interaction with the surrounding clay grains, while calcium silicates have a comparatively low viscosity and shorten the vitrification zone. It is important for the clay body of commercial wares to have a long heat range in order that pieces from different parts of the kiln may be uniform in color, size, and density. The temperature in some commercial kilns will vary from one to four cones or about 20 to 80° C.

Changes in Color.—Fired color is the most significant property in the classification of clays for commercial uses. If a clay burns to a white or light-cream color it has a possible use in whiteware and is probably refractory; if it burns buff, the clay should be tried in further tests for stoneware, terra cotta, and refractory wares, while if it burns to a dark-red or brown color, its use is limited to the dark-colored structural wares and some cheaper forms of pottery. While the clays in each class show similar characteristics in color changes throughout the firing, yet they exhibit sufficient individualities that the progress of vitrification cannot always be estimated from color alone. The color, whether red, brown, buff, or nearly white, usually deepens as vitrification progresses. The surface color of a fired piece may be different from that of the interior, due to soluble-salt action, flashing during firing, or reoxidation during cooling. The piece may be overfired and blackened on the inside and yet when cooled in a clear oxidizing atmosphere a good buff or red-brown color will be restored to the surface. The color changes in whiteware and light-buff bodies are very small. No numerical data are gained from color, and it is very difficult to assign numerical values or even accurately describe the colors obtained in fired clays. Firing is a qualitative and rough quantitative method for determining the iron content of clays.

a. The Relation between the Iron Content and the Fired Color of Clays. (1) The Amount of Iron Present.—White-burning clays may contain over 1 per cent iron oxide, or more iron than some buff-burning clays, so that the intensity of coloration is not always a direct proportion to the amount of iron present. Buff-burning clays contain from 0.50 to 5.00 per cent iron oxide with an average near 1.5 per cent. The amount of iron in buff-burning clays overlaps the amount in both the white- and red-burning varieties. Red- and dark-burning clays average from 4 to 7 per cent iron oxide and increase from this amount to low-grade iron ores. Ocher should contain 17 per cent Fe_2O_3.

A study of the three principal types of the sedimentary rocks shows that the comparatively coarse-grained sandstones have retained but small quantities of the finely divided or colloidal iron hydroxide. Likewise, the limestones, formed for the most part in clear water, have but a minimum quantity, while the bulk of the iron is carried and deposited with the fine clay sediments which later form our shales.

(2) The Size of Grain or the State of Distribution of Iron and Its Effect on the Fired Color of Clays.—Some data have been collected which indicate the ferric oxide in a very fine state of subdivision is yellow and when coarser is red.[1] Lumps of iron oxide become red on heating to low temperatures, changing to a bluish black as the temperature is increased. When added as a fine powder to clays, the color is merely darkened or browned and the bright buff or red colors of the natural clays are not produced. When added in the finely divided or colloidal form, uniform colorations free of specks appear, but the range of colors and the intensity per unit weight are not so great as those of the natural clays. The nearest duplication can be produced by grinding the colloidal iron particles with the colloidal clay particles and water in a ball mill. The most common

[1] Bancroft, W. D.: "Applied Colloid Chemistry," p. 242 (1926); Mott: *Trans. Am. Electrochem. Soc.*, **34**, 292 (1918).

method for producing or deepening the natural red and buff colors in light-colored clays is to add other clays which burn to deep-red colors. German red, Hotstetter, or similar American red clays are added to the vitrified terra cotta slips for both buff and red colors.

When iron oxide is added as granules or grains, speckles and slag spots are produced. In the Spokane district of Washington, a natural "bog iron ore" is ground and mixed with the buff- and red-burning clays, producing fused irregular spots which, when combined with the rough surface textures produce very good artistic finishes.

(3) The Influence of Accompanying Minerals on the Iron Colors of Fired Clay.

(*a*) Lime.—Lime has a well-known bleaching effect on the red colors of iron.[1] While light reds may be produced at low temperatures, or below those at which lime commences to flux with the silicates, yet, when the vitrification point is reached, the resulting colors will be brown buffs or muddy browns, if over 4 per cent of iron oxide is present. When brought to the point of complete vitrification and fusion, these turn to yellow-green colors. Green partially fused surfaces are obtained on face brick in Seattle by firing glacial clays with salt-water wood.

(*b*) Alumina.—Though not so strong in its bleaching action as lime, alumina will tend to produce buff colors with iron oxide and prevent the reduction of the buff and red or ferric forms to the brown and black or the ferrous forms. The temperature of reduction may be reduced to 1320° C. in the case of siliceous clays (low in alumina) and raised to 1390° C. in the case of the high alumina clays.[2]

Some buff and near-white firing clays are pink at low temperatures during the oxidation period. At higher temperatures this small amount of ferric oxide enters the silicate combination and the pink color disappears.

[1] Seger, H. A.: "Collected Writings," **1,** 115.

[2] Kinnison, C. S.: "A Note on the Reduction of Fe_2O_3," *Trans. Am. Ceram. Soc.*, **16,** 136 (1914). Seger, H. A.: **1,** 109. Orton, Jr., E.: "The Rôle of Iron in Burning Clays," *Trans. Am. Ceram. Soc.*, **5,** 389 (1903).

The bleaching of the iron to lighter shades may be due to the lime, to the alumina, or merely to the change in state from the uncombined Fe_2O_3 particles to a silicate glass.

(*c*) Carbon.—Orton[1] suggests the possible bleaching effects of carbon accumulations in swamps to so change the state of the iron oxide (accompanied by a reduction in the amount) that buff-burning colors results. Examples of this are found in the fire clays of the coal measures of Ohio and Pennsylvania. During the firing process, the ferrous and darker forms of iron are produced by the reducing action of unoxidized carbonaceous material.[2]

(*d*) Fluxes.—At low temperatures, when the amount of fused material is small the bright colors are produced by the suspension of the unfused Fe_2O_3 particles (Venetian red). As the temperature rises and fusion progresses, the iron is dissolved and the colors changed to yellow browns, or dark and chocolate reds and finally into blacks. Consequently, the greater the amount of fluxes present, the more rapid will be this transformation. Seger[3] attributes the light-red colors of easy-fired ware to the porous condition of the body and the consequent dilution of the red color "with air."[4] As vitrification progresses, the red particles are brought closer together, the porosity and inclosed air content reduced, and the color deepened.

(4) The Dissociation of Ferric Oxide.—When ferric oxide is heated in air, it will lose some of its oxygen and form a corresponding amount of ferrous oxide.[5] This apparently

[1] Orton, Jr., E.: *loc. cit.*, 389.

[2] Orton, Jr., E.: *loc. cit.*, 390.

[3] Seger, H. A.: **1**, 107.

[4] Compare with the streak test for the colors of powdered minerals. When powdered pigments are dried or air replaces water between the grains, the difference in the indices of refraction between the medium and the pigment has become greater, there is more light scattered from the surface of the pigment and it looks paler. Bancroft, p. 241 (1926).

[5] Hostetter, J. C., and H. S. Roberts: "Note on the Dissociation of Ferric Oxide Dissolved in Glass and Its Relation to the Color of Iron-bearing Glasses," *J. Am. Ceram. Soc.*, **4**, 927–938 (1921); Hostetter, J. C., and R. B. Sosman: "The Dissociation of Fe_2O_3 in Air," *J. Am. Chem. Soc.*, 38, 807, 1188 (1916).

dissolves in the ferric oxide to form a solid solution of Fe_3O_4 in Fe_2O_3 (see Fig. 26). The oxygen loss commences as low as 1000° C. under reduced oxygen conditions and increases with the temperature rise until melting takes place at 1590° C. At this temperature the product consists of magnetite, containing 31.1 per cent FeO. At 1300° C. the pressure of the oxygen from the ferric oxide reaches 152

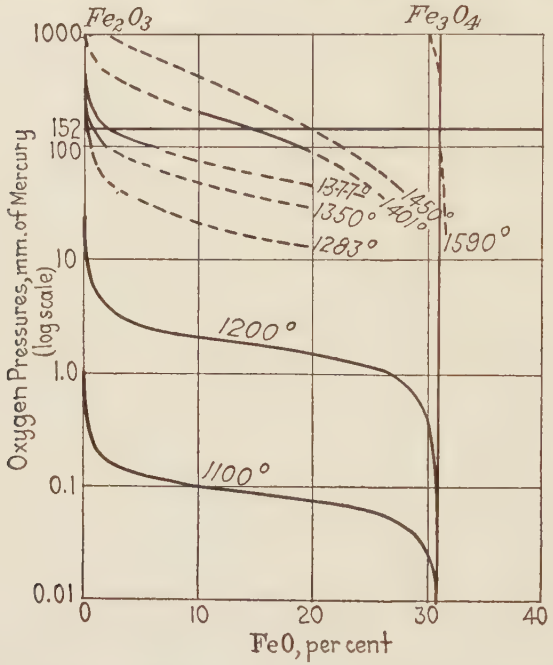


FIG. 26.—Dissociation pressure curves of iron oxides alone, in terms of pressures of oxygen. (*Hostetter, Sosman, and Roberts: J. Am. Ceram. Soc.*, **4**, 931 (1921).)

millimeters or the partial pressure of the oxygen in the atmosphere. Hence Fe_2O_3 cannot exist for any length of time at this or higher temperatures under normal oxidizing conditions.

(5) Reduction of Ferric Oxide.—The formation of ferrous oxide by dissociation is a different process from the reduction of ferric oxide by kiln gases containing carbon monoxide or hydrocarbons. These gases dilute the oxygen

present and lower its partial pressure besides removing and combining with oxygen from the ferric oxide. As shown by the curves of Matsubara, Baur, Glaessner, and Eastman (Fig. 27), the reduction of the iron oxides can take place at much lower temperatures in the presence of carbon monoxide. Eastman[1] states:

Fe_2O_3 and Fe_3O_4 at 1100° C. and above form a continuous series of solid solutions, though the indications are that at temperatures much

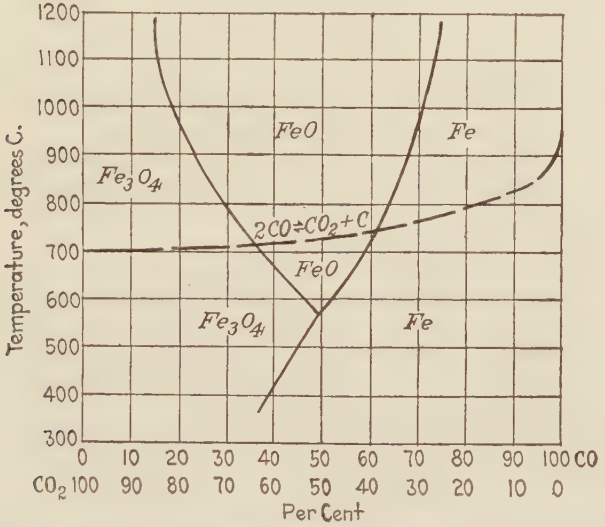


FIG. 27.—Chemical equilibrium between iron, carbon, and oxygen.

below 1000° they would not be soluble in each other in all proportions. Fe_3O_4 and FeO up to 1100° C. at least definitely do not form a continuous series of solutions, though they do dissolve to a limited extent in each other. FeO is unstable with respect to Fe_3O_4 and Fe below about 565° C. Fe_3O_4 shows an inversion in the same region.

$$2CO \rightleftarrows CO_2 + C$$

This reaction takes place towards the right only at temperatures below 1000° C. The speed of reaction is greatly affected by the temperature, for instance at 850° it is sixty-six times as fast as the reverse

[1] EASTMAN: "Equilibrium Constants and Temperature in the System Iron, Carbon and Oxygen," *U. S. Bur. Mines, Private Rept.;* CAIN, J. R., and L. ADLER: "Equilibrium Conditions in the System, Carbon, Iron Oxide, and Hydrogen," *U. S. Bur. Standards, Sci. Paper* 350 (1919).

reaction (Rhead and Wheeler). The reduced iron and the unreduced oxide both catalyze the reverse reaction. (The following reaction tends to proceed toward the right in the 900° zone: $CO_2 + H_2 \rightleftarrows CO + H_2O$.)

In Fig. 28, the clay in the raw state contained 2.33 per cent ferric iron and 5.12 per cent ferrous iron oxide. It is probable that iron carbonate, sulphate, and pyrites were present. The oxidation of the carbon and the oxidation of

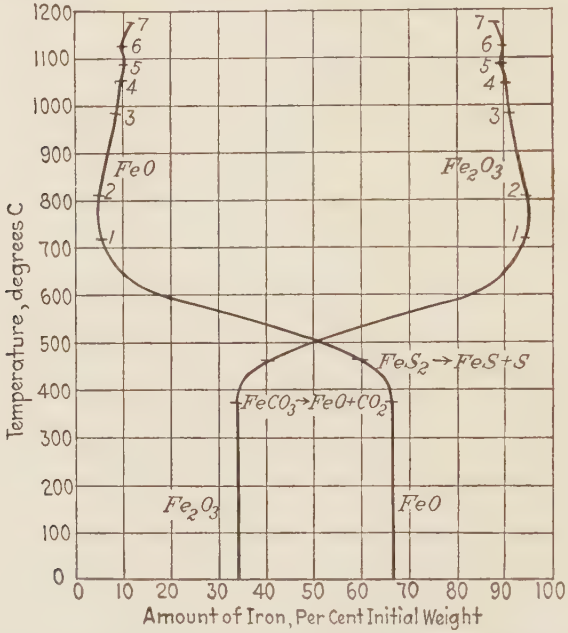


Fig. 28.—Oxidation-temperature curve of iron oxide during the firing of a red burning clay. (*Third Report, Committee on Technical Investigations, National Brick Manufacturers' Association.*)

the iron proceed almost simultaneously. It is apparent that the condition of the iron oxide remains unchanged up to 400° C., at which point the ferric oxide begins rapidly to replace the ferrous iron. Beyond 800° there is a tendency in this sample for reduction to take place. At 1350° another reverse in the condition would be expected and the ferrous iron would, undoubtedly, resume the supremacy. This is especially true in the open firing of ware in commercial

kilns about cone 7. The slow cooling of the ware under oxidizing conditions tends to restore the ferric forms.

Point (1) on the curves in Fig. 28 indicates a soft sample with a salmon color; (2) harder but still very soft, pink color; (3) still very soft and pink color; (4) red color, can still be cut with knife; (5) vitrified and dark red color; (6) darker red and vesicular structure; (7) spongy structure and maroon color.

(6) The Removal of Iron from Clays.—In the manufacture of phosgene gas, $COCl_2$, it has been noticed that siliceous clay brick were bleached to light colors.[1] Some successful experimental work has been done in removing the iron from various substances including silicates by converting the iron into volatile ferric chloride. It may be possible to convert the iron to the chloride by the introduction of some cheap chloride to the clay body or to the kiln atmosphere during firing.[2]

(7) Flashing.—Flashing is a superficial golden to red-brown color produced on a light-burning clay by subjecting it to a reducing atmosphere at high temperatures, followed by cooling in oxidizing conditions. It is the partial reoxidation of the dark ferrous silicates or oxide to buff ferric forms. It requires reduction followed by oxidation. Reduction may be used throughout the entire burn and followed by an oxidation period during cooling; it may be used at the high temperatures only; or successive alternate reduction and oxidation treatments may be given.

According to Henderson,[3] the surface flash contains red and yellow hexagonal plate-like crystals possessing magnetic properties. They are similar to those present in the salt glazes of sewer pipe.

Trials drawn during the cooling process show progressive increase in the number of crystals. The parts of the brick not exposed to the flame and yet in contact with the

[1] Washburn and Libman: *J. Am. Ceram. Soc.*, **3**, 635 (1920); Baskerville, C.: *Science*, **50**, 443 (1919).

[2] U. S. Patent No. 1585826 adds a basic solution of aluminum chloride.

[3] Henderson, H. B.: "Some Phenomena in Glaze Reduction," *J. Am. Ceram. Soc.*, **1**, 148–159 (1918).

general reducing conditions of the kiln are not flashed. The local heating effect of the surface by the direct flame apparently causes surface fusion which is necessary for the later growth of the crystals. A flashed brick when refired under oxidizing conditions returns to the natural oxidized buff color. Refiring under reducing conditions retains or develops the original flashed color if followed by oxidized cooling. Henderson[1] suggests that the iron may give greater coloring effects when in the crystalline than in the amorphous condition.

It would be interesting to study the effect of sublimation of the iron salts and the formation of the iron-silicate crystals from the vapors.

According to Bleininger,[2] the degree of flashing depends on five factors:

1. Chemical composition of the clay; the amount, distribution, and character of the iron and associated minerals.
2. Physical condition of the clay.
3. Temperature of burning.
4. Degree of reduction.
5. Rate of cooling as being equivalent to rate of oxidation.

Such fluxes as lime and the alkalies assist in flashing. A small per cent of common salt or finely ground blast-furnace slag aids in producing flashes. Siliceous clays take a flash more easily than high aluminous clays. Vitrification takes place easier and at a lower temperature with stiff-mud ware than with dry presses, and the former is easier to flash. Fine grinding usually gives more uniform flash colors than coarse grinding.

In flashing, the iron is chemically united with silica to form a silicate insoluble in acids. It is not simply a case of reduction and oxidation of free oxide, otherwise flashed surfaces could be produced at low temperatures and such is not the case. According to Baur and Glaessner's curve (Fig. 27) for the reduction of ferric oxide, it will be necessary

[1] *Loc. cit.*

[2] BLEININGER, A. V.: "Notes on Flashing," *Trans. Am. Ceram. Soc.*, **2**, 74 (1900); and "Effect of Heat on Clays," p. 46, T. A. Randall and Company, Indianapolis (1911).

to go to 1100° C. before Fe_2O_3 can be reduced to FeO with an atmosphere of 15 per cent CO and 85 per cent CO_2. Additional hydrocarbons in the gases no doubt assist in the reduction. For lower temperatures, the content of CO must be much greater and no doubt too great for the ordinary ceramic kiln. Bleininger's[1] reducing burn gave only 13 per cent CO. With his clay he found that reduction equal to 80 per cent air was sufficient with a maximum temperature of 1190° C. Baur and Glaessner's curves show why it has been so difficult to keep clay wares in the reduced condition in commercial operations, where a long oxidizing cooling period above red heat follows the firing period. The CO content at 700° C. must be 36 per cent with no oxygen present in order to keep the FeO from returning to Fe_3O_4 and Fe_2O_3. In small laboratory kilns the cooling period is much shorter.

Sulphuric acid tends to give a pinkish color which may persist after reduction and oxidation. Different coals give different results in reduction. The long-flamed smoky types are better than the short-flamed open-burning coals. The size of iron spots is increased by reduction. The longer cooling period under oxidizing conditions from the end of firing after reduction to about 700° C. will deepen the flash color. Trials drawn immediately after firing will show no flash, only a gray color due to reduction. The flash gradually develops in the next 15 hours of cooling in commercial kilns.[2]

(8) Summary of the Fired Colors of Clay Due to Iron.—Hermann A. Seger[3] gives the following classification:

1. High iron, 5 to 9 per cent.
   Low alumina, 10 to 22 per cent.
   No lime.

Under oxidizing conditions all shades of red are produced up to complete vitrification, where they darken. No

[1] *Loc. cit.*

[2] Orton, Jr., E.: "The Rôle of Iron in Clay Burning," *Trans. Am. Ceram. Soc.*, **5**, 425 (1903).

[3] Seger, H. A.: "Collected Writings, Colors of Brick," **1**, 106.

trouble is experienced with sulphurous or sulphuric acid gases. Under reducing conditions, browns, dark grays, and black appear. Sulphuric acid gases counteract the reducing conditions and help hold red and violet colors, provided oxidation follows. Intense reducing conditions are used in Europe for the blue-smoked Staffordshire brick and Dutch roofing tile by adding oil to the tightly closed kilns during cooling. Reoxidation tends to restore red colors.

2. High iron, 6 per cent.
   High lime, 14 per cent CaO.
   Low alumina, 10 to 22 per cent.

Creams and buffs (rather a poor variety) are produced at low temperatures and greenish brown and black colors when vitrified and fused. Sulphuric acid gases tend to prevent the bleaching action of the lime.

3. Fairly high in alumina, 19 to 26 per cent.
   Moderate iron oxide, 1.5 to 3.0 per cent.

These burn to buff colors and are used in face brick, terra cotta, stoneware, and for No. 2 fire brick. At high temperatures or under reducing conditions any pyrite boils out in surface pimples and blotches. These are the clays ordinarily used for flashed wares.

4. High alumina.
   Low iron.

Examples: kaolins, ball clays, and No. 1 fire clays. These are pink or white at low temperatures, changing to bluish or grayish white under reducing conditions at high temperatures or cream under oxidizing conditions. The higher the iron content the closer do they approach class 3 in color.

b. Effect of Titanium Oxide on the Color of Clays.—While small quantities of titanium oxide are present in most clays, the amount is so small and the coloring power so feeble that the color is but little affected. Titanium oxide occurs as rutile, TiO_2, or ilmenite, $FeOTiO_2$, and produces light-buff or straw colors when mixed with white clays or

glazes. According to Audley,[1] rutile exaggerates the red coloration due to iron.

c. Effect of Manganese Oxide.—Pyrolusite, MnO_2, is an uncommon ingredient of natural clays, though it is a common coloring agent for artificial bodies and glazes. It produces browns and, when sufficiently concentrated, blacks. The jet-black spots of much face brick and terra cotta have been made with manganese dioxide.

d. Colors from Mixtures of Clays.—Hand samples from the face of a bank may show buff-burning material, but when the whole face is mixed and ground together in the commercial process, the quantity of dark-burning material, which was not included in the hand sample, may be so great that the mixture will burn red or brown. The bodies of residual clays of eastern Washington and northwestern Idaho often contain a number of colored clays in the same bank. White clays will lie alongside dark-burning clays, so that the commercial mixture when fired will show but a few white spots in a dark ground mass. Likewise, percolating waters may carry iron salts into the fissures and cracks of a bedded secondary clay with the result that the fired color of the pulverized mixture is much darker than that of hand samples taken from the same face. For this reason it is necessary to follow some systematic method of sampling which will include all portions of the face to be used and which will give at least roughly, the proportional amount of each variation. See the sampling methods of the American Ceramic Society.[2]

In blending two or more clays the physical properties of the mixture will practically follow the arithmetical proportion of the properties of the individual clays. In a manner similar to the blending of water colors, the different-colored clays can be blended to produce new colors. In this case the two following points should be remembered:

[1] Audley, J. A.: "Silica and Silicates," p. 76, D. Van Nostrand Company (1921).

[2] "Standard Methods of Testing Clays," *Am. Ceram. Soc. Year Book* (1921–1922).

1. A red- or dark-burning clay is far more active as a coloring agent than a white- or buff-burning one when the percentage amounts are considered. In other words, it is easier to change the color of white clay to buff, or of buff clay to brown, than it is to lighten the color of a dark-burning clay with a lighter one. A few drops of ink will color a quart of water, but a large amount of water will be required to dilute this mixture back to the clearness of the original.

2. The fineness of the ground materials or the degree of intimacy of the mixing has an important effect on the resulting color. The finer the individual grains of the clays, the less speckled and the more uniform will be the blended color. The dry-pressed product of a dry-ground mixture of buff- and red-burning clays will show the individual grains of buff and red clays on the surface of the burned brick and the combined color will usually be lighter than the same mixture prepared by the plastic or slip method. In the latter cases the disintegrating action of the increased amount of water has separated the small lumps of semidry clay into much finer particles and has mixed them better so that the color will show the result of the greater staining effect of the red clay. The action of the die on the column of clay in the auger machine tends to coat all the larger particles with this fine material and thus gives the color of the finely divided mass. When shale or hardened clay materials which do not disintegrate easily in water, even though ground in a dry pan, are mixed with soft clays which do slake easily, the latter will have the coloring advantage. The finely divided plastic particles of the soft clay will coat the larger particles and hide their color.

Changes in Hardness.—An accurate description of hardness is rather difficult to make. It depends on the density, tensile strength, and shear strength of the material[1] and has been defined as resistance to permanent deformation.[2] The scratching test for relative hardness must be

[1] UPTON: "Materials of Construction," 4 (1916).

[2] JEFFRIES and ARCHER: "The Science of Metals," p. 403 (1924).

used with caution and under specified conditions, for with many pairs of substances either may scratch the other when used as a point or cutting edge on the plane surface of the other and different results are obtained when an edge is cut.[1]

No satisfactory apparatus has been devised for grading fired clay wares according to hardness. The knife test is good enough for rough work with clays and will discriminate between those bodies softer than steel. In the abrasive industry a similar tool in the hands of an experienced operator is used to grade the hardness or bond of the grinding wheels. Most common brick can be cut rather easily with the knife. Terra cotta is steel hard or nearly so, and the well-vitrified products like paving brick and porcelains are much harder than steel. A body usually has from 10 to 15 per cent water absorption at the time it becomes steel hard.

Changes in Strength.—While the strength of some ceramic bodies such as the silica brick, mullite wares, etc. is due to interlocking crystallization, vitrified-clay wares depend on the binding strength of cooled glass films. The strength of fired-clay bodies has not been generally used in determining the degree of vitrification. Satisfactory standards have never been devised for all classes of ware. Variations due to imperfect structure require the averaging of a large number of results. The apparatus required for such testing is not so simple as that required for absorption or porosity. For such ware as structural brick, sewer pipe, and drain tile crushing-strength specifications have been prepared by the American Society for Testing Materials. The transverse breaking strength is almost universally used for general strength testing of test pieces of laboratory size.[2] This gives more uniform results than either the

[1] BANCROFT, W. D.: "Applied Colloid Chemistry," p. 183, McGraw-Hill Book Company, Inc. (1926).

[2] Transverse strength machines for laboratory use:

a. BLEININGER, A. V., and W. L. HOWAT: "The Compression, Tensile and Transverse Strength of Some Clays in the Dried State," *Trans. Am. Ceram. Soc.*, **16**, 275 (1914).

crushing or tensile tests and can be conducted more easily than the former. Strength determinations quickly indicate overfiring when it is caused by the development of a vesicular structure. Strength determinations are erratic when made on pieces drawn hot from the kiln and cooled quickly. Slow annealing is necessary to avoid brittleness and the subsequent checking and cracking.[1] Most clay products if carried to a knife-hard condition will carry any ordinary structural load. Many wares such as drain, tile, and common brick are not fired to a knife-hard condition and yet give satisfactory service.[2]

Changes in Specific Gravity.—Specific gravity is the weight per unit volume expressed in terms of the density of water. Using the same dried weight of the fired piece, there may be three different specific gravity values: (1) the *true specific gravity,* using the actual volume of the clay mass after both the sealed and open pores have been eliminated by fine grinding; (2) the *apparent specific gravity,* using the apparent volume or that consisting of the sealed pores plus the clay mass (obtained by subtracting the volume of the open pores from the exterior volume); and (3) the *bulk specific gravity,* using the bulk or exterior volume. The changes in true specific gravity are not well understood and comparatively few data on this subject are to be found. It is affected by the specific gravity changes of the mineral constituents and thus often produces results apparently having no connection with the progress of vitrification. As

b. MacMichael, R. F.: "The Testing of Clay," *Trans. Am. Ceram. Soc.*, **17,** 651 (1915).

c. Testing apparatus of the Tinius Olsen Testing Machine Company, Philadelphia, Pa., and the Riehle' Brothers Testing Machine Company, Philadelphia, Pa.

d. U. S. Bureau of Standards transverse-strength apparatus for full-sized brick, *Bull. Am. Ceram. Soc.*, **4,** 407 (1925).

[1] Houldsworth, H. S.: "Note on the Influence of Rapid Cooling on the Reversible Expansion of Fire Clay," *J. Soc. Glass Tech.*, **8,** (29) 30 (1924).

[2] The U. S. Bureau of Standards has recently developed a machine for determining the resistance to abrasion of different flooring materials. See: Geister, Carl H.: "An Accelerated Abrasion Test," *J. Am. Ceram. Soc.*, **9,** 121 (1026) and "Endurance of Flooring Materials," *ibid.*, 126.

a mineral changes from the crystalline to the glassy or melted condition, its specific gravity decreases, while as vitrification progresses in a clay body the bulk and apparent specific gravities increase in value. The apparent specific gravity should equal the true specific gravity until some of the interior pore spaces are sealed by partial fusion. Both the apparent and bulk specific gravity data will indicate swelling or development of vesicular structure, but the numerical values are not so large as those of volume shrinkage or porosity.

The factors which affect the specific gravity of clays during firing are as follows:

1. Inversion.
2. Fusion.
3. Chemical reactions.
4. Crystallization.
5. Change of state.
6. Pore space.
7. Formation of blebs.

Spurrier[1] has reported a unique specific gravity determination for quickly and economically grading large numbers of fired electrical porcelain pieces into underfired, properly fired, and overfired groups. Dense solutions having a specific gravity around 2.7, such as Thoulet's solution and mercuric chloride are used. The pieces are placed in a wire basket and immersed in a solution of such a specific gravity that the underfired piece sinks while the properly fired piece just floats. In the second solution the properly fired pieces sink and the overfired ones float. A difference of 0.001 in specific gravity can be distinguished in this way.

The true specific gravity curve of the Galesburg shale (Fig. 29), shows a steady increase in specific volume which is complete only at the fusion point. This action is independent of the change in exterior volume which decreases up to cone 1 and increases at higher temperatures. Similar

[1] SPURRIER, H.: "The Use of Dense Solutions in Determining the Structure of Porcelains," *J. Am. Ceram. Soc.*, **1**, 287 (1918).

results were obtained with five other surface clays and shales examined by Bleininger and Montgomery.[1]

NOTE.—Beyer and Williams[2] found that the true specific gravity had decreased with twenty-eight out of thirty-two clays on burning. Ogan[3] found that the true specific gravity remained practically constant for two fire clays at approximately 2.62 up to cone 7 and then increased slightly at cone 13. Lovejoy[4] and Barringer[5] give settle curves for brick kilns. The measurement of settle gives the linear shrinkage or expansion for the column of brick piled in the kiln. Most of the curves show a definite expansion

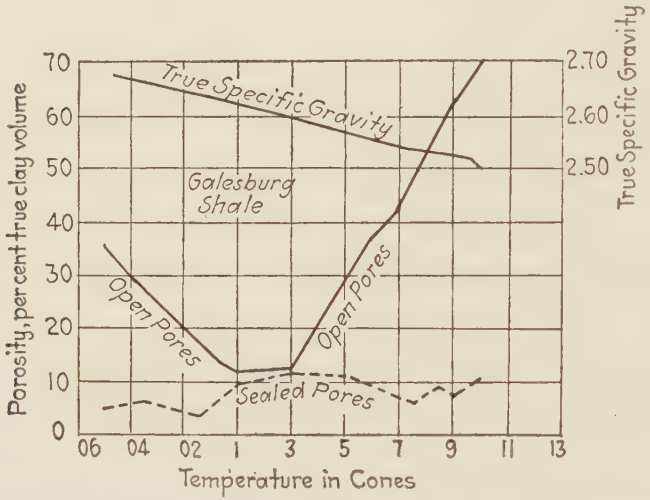


FIG. 29.—True specific gravity, open and sealed pore space. (*Bleininger and Montgomery: "Effect of Overburning upon Clays," T.A.C.S.*, **15**, 76 (1913).)

near the dehydration temperatures before the vitrification shrinkage is obtained. A temporary thermal expansion is noted when fired clay wares are reheated below their shrinkage temperatures. Knote[6] gives a diagram showing the changes in specific gravity for plastic and flint fire clays. The true specific gravity rises from 2.6 (raw clay) to about 2.62 at 450°; drops

[1] BLEININGER, A. V., and E. T. MONTGOMERY: "The Effect of Overburning upon the Structure of Clays," *Trans. Am. Ceram. Soc.*, **15**, 71 (1913).

[2] BEYER and WILLIAMS: *Iowa Geol. Survey*, **14**, 116 (1903).

[3] OGAN, J. M.: "Cause of Permanent Expansion in Firebrick," *Trans. Am. Ceram. Soc.*, **13**, 610 (1911).

[4] LOVEJOY, ELLIS: "Settle Curves for Brick Kilns," *Trans. Am. Ceram. Soc.*, **7**, 422 (1905).

[5] BARRINGER, L. E.: "Measurement of Settle in Brick Kilns," *Trans. Am. Ceram. Soc.*, **7**, 409 (1905).

[6] KNOTE, J. M.: "Chemical and Physical Changes in Clays Due to Heat," *Trans. Am. Ceram. Soc.*, **12**, 262 (1910).

to 2.49 at 550°, from where the apparent specific gravity rises to 2.65 for the plastic and 2.71 for the flint fire clays. As soon as definite vitrification begins, the apparent specific gravity drops slowly toward 2.40, though in one case this occurs without much evidence of vitrification. (Compare with Fig. 23, which shows the specific gravity curve for kaolin at dehydration temperatures.)

Changes in Volume.—The contraction in volume and the closing of the pore spaces are not due entirely to fused and liquid matter, since colloidal material will condense on heating without fusion. This is illustrated by the shrinkage of amorphous alumina and magnesia at high temperatures.[1] The amount of drying and firing shrinkage and the progressive change in shrinkage during firing are two important points to consider in testing clays for manufacturing purposes. A high shrinkage usually indicates a strong, dense body, which, however, may be ruptured with cracking.[2] A small shrinkage indicates that there is present a large quantity of non-plastic, non-shrinking material (sand or grog), that the clay has not been carried to its vitrification temperature, or that the clay has been carried beyond the temperature at which the volume was a minimum and the sample has bloated or swelled. In any case, the body will be porous and usually weak. Excessive shrinkage indicates that the use of non-plastics or precalcined material will be necessary to maintain the proper shape and size without warping, bending, or cracking. The progressive change in shrinkage reveals the best firing temperature. For exact commercial work, it is not safe to fire to a temperature at which the rate of shrinkage is still high, otherwise the temperature variations in commercial kilns (often four cones) will produce ware of considerable variation in size. A temperature located within a period of low rate of volume change should be selected to maintain uniform sizing of commercial products. This is a very important consideration for wares in which the units must

[1] Brown, G. H., and G. A. Murray: "The Function of Time in the Vitrification of Clays," *Trans. Am. Ceram. Soc.*, **15**, 193 (1913).

[2] A clay with a high pore space in the dried condition must have a high-fired shrinkage to produce a dense and vitrified structure.

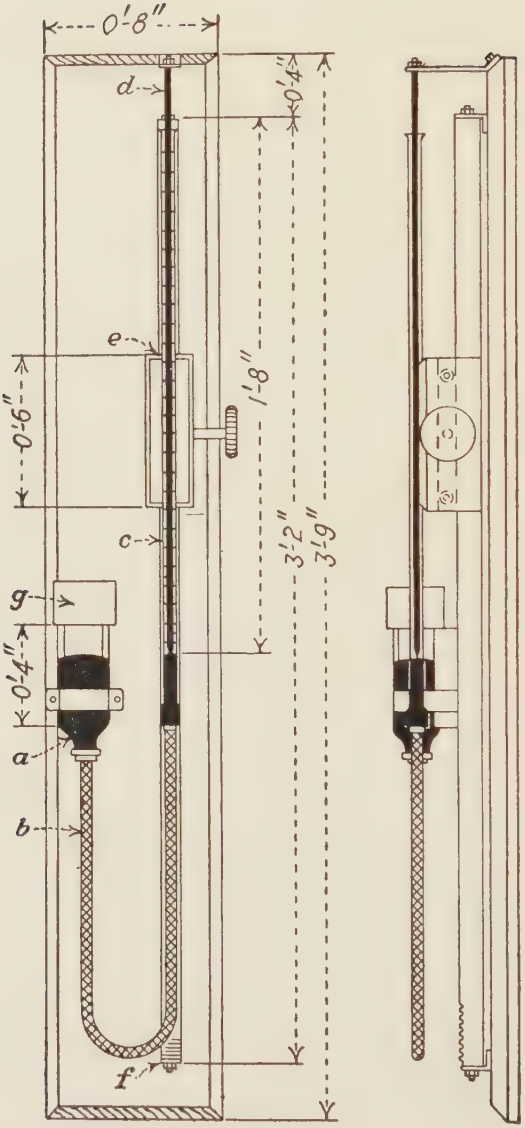


FIG. 30.—The Goodner mercury volumeter. *a* is the mercury reservoir where the sample is placed; *b*, pressure rubber tubing; *c*, burette which can be raised and lowered on the rack; *d*, copper pointer fastened at top and projecting into the burette; *e*, framework for the pinion operating vertically on the rack; *f*, the rack which is fastened to the foundation board; *g*, the iron weight for holding sample beneath the mercury bath. The free surface of mercury in the reservoir should equal the mercury surface area in the burette. (*Goodner, E. F.: J. Am. Ceram. Soc.*, **4**, 294 (1921).)

fit accurately in a wall facing, such as terra cotta, porcelain floor and wall tile, and even refractory shapes.

a. Measuring Volumes.—One of the simplest methods of measuring the volumes of small briquettes about 1⅛ by 2 inches is the Goodner mercury volumeter(8). It can be used for plastic, dry, or fired bodies without preliminary soaking in liquids (see Fig. 30). The volume of mercury displaced by the test piece is read at once in the side burette. Westman(10) has also used mercury in determining the volumes of full-sized brick. He finds the weight necessary to hold the sample submerged in a bath of mercury (see Fig. 31). Hartmann, Westmont, and Morgan(9) determine the volumes of large samples by finding the volume of zircon sand (124 to 148 mesh) necessary to fill the remainder of a steel box after the sample has been inserted.

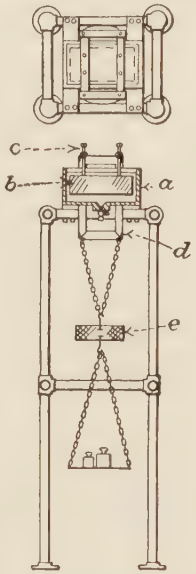


FIG. 31.—The Westman mercury balance. *a* is the mercury trough of cast iron, 10 by 5½ by 5⅝ inches inside; *b*, the brick immersed in the mercury; *c*, four bolts in the saddle for holding the brick under the mercury; *d*, the lower part of the saddle, *e*, a permanent weight adjusted to make the weight of saddle, scale pan, and chains plus weight equal to 14 kilos. (*Westman, A. E. R.: J. Am. Ceram. Soc.*, **9**, 314 (1926).)

References on Volumeters

1. "The Seger Volumeter," *Iowa Geol. Survey, Ann. Rept.*, **14**, 115 (1903).
2. SCHURECHT, H. G.: "Schurecht's Pycnometer Volumeter," *J. Am. Ceram. Soc.*, **1**, 556 (1918).
3. SHAW, J. B.: "The Shaw Direct Reading Pycnometer," *J. Am. Ceram. Soc.*, **2**, 487 (1919).
4. "Hubbard and Jackson Volumeter," *Proc. Am. Soc. Testing Materials*, **16**, 378 (1916).
5. STALEY, H. F.: "Staley Volumeter," *U. S. Bur. Standards, Repts on Staley Volumeter* (1919).
6. SPURRIER, H.: "Spurrier Volumeter," *J. Am. Ceram. Soc.*, **3**, 400 (1920).
7. SCHURECHT, H. G.: "Schurecht Overflow Volumeter," *J. Am. Ceram. Soc.*, **3**, 730 (1920).
8. GOODNER, E. F.: "Goodner's Mercury Volumeter," *J. Am. Ceram. Soc.*, **4**, 288 (1921).
9. HARTMANN, M. L., O. B. WESTMONT and S. F. MORGAN: "The Determination of the Bulk and Pore Volumes of Refractory Materials," *J. Am. Ceram. Soc.*, **9**, 298 (1926).
10. WESTMAN, A. E. R.: "The Mercury Balance—"An Apparatus for Measuring the Bulk Volume of Brick," *J. Am. Ceram. Soc.*, **9**, 311 (1926).

b. The Veritas Firing Rings.[1]—The veritas rings are refined draw trials made of a standard, unfired, whiteware body composition. The rings, 2.5 inches in diameter with a hole of about 0.85 inch, are drawn from several important points in the kiln at various temperatures and the linear shrinkage magnified and measured in a simple lever and scale device. The same principal was devised by Josiah Wedgwood about 145 years ago and is still paralleled by the common draw trials of everyday practice. Such draw trials indicate the progress of firing at any time after shrinkage starts and in any part of the kiln which can be reached by a rod. Draw trials also indicate the heat work done upon the body. The rate of firing may be accelerated during the period when little contraction is taking place and retarded when shrinkage is proceeding at its maximum rate. Tests by the above authors show that the rings are similar to cones in that they do not indicate exact temperatures. Also, the more rapid the rate of firing, the higher must be the temperatures corresponding to different shrinkage numbers and *vice versa*. It would be advisable to make the rings of the same body as the ware being fired.

Changes in Porosity. *a. Nature of Open and Sealed Pore Spaces and Their Measurement.*—The degree of porosity in fired ceramic ware is a most important property because of its relation to strength, bulk density, permeability, and thermal and electrical conductivity, and because of its resistance to the following: weathering, thermal shock, abrasion, erosion, slagging, discoloration, efflorescence, chemical attack by gases, liquids, or fungus growths.[2]

Washburn[3] classifies pores as follows:

1. The closed, sealed, or bubble pore.
2. The channel pore.

[1] Bleininger, A. V., and G. H. Brown: "The Veritas Firing Rings," *Trans. Am. Ceram. Soc.*, **16**, 222 (1914); Broga, W. C., and C. J. Hudson: "A Convenient Instrument for Making Shrinkage Measurements," *J. Am. Ceram. Soc.*, **5**, 34 (1922).

[2] Reference 10, p. 187, and Scott, James: "Tile Fungus," *Brit. Clayworker*, **18**, 138 (1920).

[3] Reference 10, p. 187.

3. The blind-alley pore.
4. The loop pore.
5. The pocket pore.
6. The micropore.

The *pocket pore* is a large bubble pore which has a small opening. The micropore is so small that it cannot be filled by liquid absorption and approaches the intermolecular pore space. *Cracks* and *holes* are openings in the body which are too large to be counted as pores. The size of the spaces classified as pores will vary with different types of ware, however. For instance, the pore spaces of several types of insulating brick, which have been formed by the burning out of large sawdust or cork particles are entirely too large to be classed as pores in the dense vitrified wares. The apparent magnitude of the open pore space will vary with the method of porosity determination and the fluid or gas employed.

b. Permeability should be limited to the ease with which a liquid flows through a body from one side to the other.[1] It can be determined by finding the rate of flow of a standard liquid or gas under specified conditions of viscosity, temperature, and pressure through a unit area and thickness of the body(23). The channel pores are the active agents in this case.

c. Penetrability is qualitatively defined by Washburn[2] as "the ease with which a liquid is drawn into the pores of the body by capillary action, without attendant chemical action between the body and the liquid." The quantitative amount absorbed will depend on the liquid, its viscosity, temperature, the time employed, the amount of surface in contact with the liquid and the position of the surface with respect to the fluid level. The large channel pores would be the only ones completely filled by absorption methods, and with some sizes and positions of the test pieces, such as full-sized brick standing on end in a shallow bath of water, capillary action would not be able to draw the water to the top and completely fill all the large channel pores.

[1] Reference 10, p. 187. [2] *Loc. cit.*

The amount of liquid which penetrates a porous body is proportional to the square root of the time of soaking and to the square root of the ratio between the surface tension of the liquid and the viscosity of the liquid for all cylindrical pores except those of molecular dimensions.[1]

d. Nature of Sealed Pores and the Vesicular Structure.—It is practically impossible to fire the dense vitrified wares, such as paving brick, sewer pipe, electrical porcelain, stoneware, glass pots, etc., without some vesicular development. Open porous bodies, such as fire brick and terra cotta, which have been grogged and are not fired to a dense vitrification contain the minimum sealed-pore space. Gases are being evolved at the high temperatures, and if a body is near its vitrified condition or if enough fluid material has developed to cause it to vitrify, at least some of the gas bubbles will be retained. Open porous bodies allow them to escape. The gases evolved from various sources may consist of:

1. Entrapped air.
2. Steam.
3. Sulphur dioxide and trioxide.
4. Carbon dioxide or monoxide.
5. Oxygen.
6. Hydrocarbons absorbed during firing.

The "bleb" or vesicular structure develops to the greatest degree in the fine-grained, dense bodies and so can be partially relieved in the case of indurated or hard shales by coarser grinding and in the case of soft, fine-grained clays by the introduction of porous calcined material or sometimes sand. These of course weaken the body. While bloating is due to the expansion of entrapped gases in a semiviscous body, we can divide it into two classes. The first is due to improper oxidation and can be avoided by giving sufficient time at temperatures below the vitrification period for the escape of the gases, chiefly formed from the carbon, sulphur, and carbonates. When improperly oxidized, the interior of the body will show the black, spongy core of reduced iron silicates. The second class of bloating or vesicular structure is due to gases which are not

[1] Reference 11, p. 187.

formed until temperatures are reached which are higher than the beginning of vitrification. The most common of these is the sulphur dioxide or trioxide formed from the decomposition of calcium sulphate. Carbon and sulphur may be deposited in the porous body before vitrification by heavy reduction and then produce gas bubbles after the surface is sealed over. Pin holes and blisters in glazes may likewise be produced in this manner. The color of the interior of the body is grayed throughout by reduction. Molding defects, such as air pockets formed by lamination or improper hand pressing, often provide a weakened structure and an interior cavity for the collection of gases, which expand to large blisters. These are seen in sewer pipe, stoneware, and dense porcelain wares. The walls of such pore spaces must be strong enough to resist the pressure of the absorbed fluids or gases.

The minimum absorption for the Galesburg shale (Fig. 29) occurs between cones 1 and 3. The open pore space has decreased from 30 per cent at cone 05 to practically zero at cone 3. The sealed pore space decreases to cone 1, remains fairly constant to cone 3, and then increases rapidly at the higher temperatures, due to the development of vesicular structure. It is not safe to fire the clay above cone 1. Above cone 3 the sealed pores again decrease although the total pore space has increased. The viscosity of the fluid portion of the body is low enough not only to allow the swelling of the gas vesicles but also to permit them to communicate with the surface so that water will penetrate when tested later. Below cone 3, the structure is too rigid for the vesicles to burst, though they are enlarging within the mass.

e. Measurement of Porosity.—Porosity may be expressed in three ways:

1. *Per cent absorption* or the weight of water absorbed into the open pores in terms of the dried weight.

2. *Per cent apparent porosity* or the weight of the water absorbed into the open pores in terms of the exterior volume. (C. G. S. system.)

3. *Total porosity* or the volume of both sealed and open pores expressed in terms of weight or volume. (No standard definition.)

The first two are the more commonly used. The total pore space may be determined by obtaining the true specific gravity of the ground powder and from this the true volume of the clay mass. The difference between this and the apparent volume (sealed pores plus clay mass) gives the volume of sealed pores to add to the open pores for total pore space.

The per cent apparent porosity is from 1.5 to 2.5 times that of the per cent absorption and is more commonly used for technical work and for small samples the volume of which can be measured with one of the several improved types of volumeters. For larger samples, such as full-sized brick, it is common practice to use the per cent absorption test, as the only determinations needed are those of weight. Per cent absorption indicates swelling only when the gas vesicles have broken through the surface and have increased the water absorption, for the weight will remain fairly constant until a large volume of gas has been evolved. If the bulk volume should increase due to the development of unbroken gas blebs, the per cent apparent porosity will decrease. Hence, volume shrinkage and possible fired-strength curves must be watched for the first evidences of vesicular development.

f. Saturation of Clay Wares by Complete Immersion.[1]— The amount of liquid absorbed by a porous solid when completely immersed in a liquid will vary with the character of the pore space, the viscosity of the liquid, the surface attraction of the solid for that liquid, the rate of the solution and diffusion of the entrapped air in that liquid, and the time employed. With simple immersion without boiling, pocket pores with small openings are filled very

[1] The following notes on the determination of porosity are taken from references 10 to 15 by E. W. Washburn and others in the ceramic laboratory of the University of Illinois. They present the best series of work on the application of refined physical chemical methods to an old ceramic problem.

slowly. Complete saturation cannot be obtained in any reasonable period of time by immersion in water alone when the pore spaces are small. A vacuum treatment insufficient to boil water is not so effective as boiling in air.

Washburn[1] found no appreciable error by the absorption of *dry* air by any of his fired-clay pieces. Fired-clay wares will take *water* from calcium chloride and from sulphuric acid. When in contact with moist air, a layer of strongly adsorbed water vapor about one molecule deep will be held onto the surface of the fired clay. This cannot be removed by the two dehydrating agents mentioned above. An appreciable error is found when fired clay wares, especially those which have not been well vitrified, are left in contact with moist atmosphere.

The usual method for water absorption is from 1 to 5 hours boiling in air, depending on the size of the test piece. Washburn[1] found the following errors in this treatment:

TABLE XXII.—ERRORS OF THE USUAL BOILING IN AIR TREATMENT

	Per Cent of True Per Cent Absorption by Weight
POSITIVE ERRORS	
From rehydration on 3 hours' boiling	2
Rehydration on prolonged boiling	1 per day
NEGATIVE ERRORS	
Material dissolved on 3 hours' boiling	2
Adsorbed moisture from cooling in moist air	2
Incomplete saturation by boiling for only 1 hour	2 to 10

The above errors are not large enough to interfere with the ordinary porosity determinations for structural wares. The following methods are given for accurate work.

Washburn's Recommended Method of Cooling Fired Test Pieces.—For a fairly constant and yet accurate "dry" weight, allow the fired test piece to remain in contact with moist air for a short time and then place in a desiccator over 95 per cent sulphuric acid until the weight is constant (2 to 3 hours).

[1] The following notes on the determination of porosity are taken from references 10 to 15 by E. W. Washburn and others in the ceramic laboratory of the University of Illinois. They present the best series of work on the application of refined physical chemical methods to an old ceramic problem.

Washburn's Recommended Method for Accurate Water Absorption.—The above errors of rehydration and solution are avoided by omitting boiling and stirring and by the use of cold water. The dry test pieces are placed in a vacuum chamber and the pressure reduced (to about 7.6 millimeters mercury for 1 per cent accuracy) until equilibrium conditions are attained. Air-free, cold, distilled water is then admitted to cover the test pieces, and the vacuum is broken immediately. The test pieces are allowed to soak (a few minutes for porous to 5 hours for dense wares) until the water has completely penetrated the pores. When the trials are removed, they should be wiped with a very damp towel or immersed in mercury to remove the surface water before weighing. Evaporation during weighing may be prevented by inclosing the test pieces in a weighing tube. With less effective vacuum apparatus, the second-best method consists of boiling in vacuum for the minimum time to obtain the desired accuracy. The employment of pressures of several hundred atmospheres in the first method will greatly reduce the time of soaking. This is the only method found for introducing a liquid into the very fine pores of very dense porcelain bodies.[1]

g. Absorption Method for Highly Vitrified Bodies.—Porcelains for electrical insulation often have an absorption less than 0.01 per cent. A qualitative test has been developed to determine the resistance to the penetration of dye under high pressures. The samples are immersed in a solution of fuchsine dye in wood alcohol, and the pressure is raised to 200, 250, or 7,000 pounds per square inch and held there for from 2 to 12 hours.[2] The slightest measurable porosity will show a penetration of several tenths of an inch. For high-tension work any penetration of dye means rejection of the ware.

h. The Use of Petroleum Products as Absorption Liquids.[3] The American Society for Testing Materials recommends the use of kerosene in place of water in a 4-hour soaking at 25° C. under a vacuum of 24 inches of mercury. Kerosene is not so good as other petroleum liquids, for its penetrativity is only about one-twentieth that of water at ordinary temperatures. Paraffin was found suitable for absorption work, but vaseline is preferable because it undergoes no change of phase on cooling. The results obtained with vaseline were about 2.3 per cent higher than

[1] CUDE and HULLETT: *J. Am. Chem. Soc.*, **42**, 400 (1920).

[2] PEASLEE, W. D. A.: "Testing of Porosity of Electrical Porcelain," *Am. Soc. Testing Materials*, **20** (II), 495–499 (1920). Reference 15, p. 535.

[3] References 12 and 13.

those obtained with water.[1] The advantages of the use of vaseline are as follows:

1. Absence of slaking action on raw, unfired clay.
2. Practically no solvent action of clay.
3. No chemical combinations.
4. Less tendency to be adsorbed on the surface than water.
5. Vaseline becomes stiff at room temperatures and can be wiped from the surface of the test piece without draining any of the pore spaces. This is especially suited for bodies containing very large surface pores.

i. Determination of Porosity by the Gas-expansion Method.[2] The open-pore volume is measured by determining the

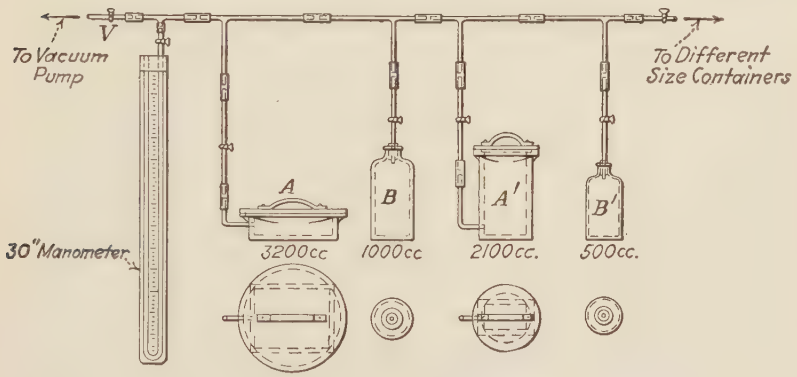


FIG. 32.—Gas porosimeter. (*Hartmann, Westmont, and Morgan: J. Am. Ceram. Soc.*, **9**, 301 (1926).)

fall in pressure when the air from the pores is allowed to expand into a measured volume under a definite pressure. Advantages: (1) it is rapid; (2) it can be used to determine both pore volumes and bulk volumes; (3) it is applicable to all types of porous bodies or granular materials; (4) the degree of accuracy is higher than that of any other method; (5) there are no weighings to be taken; and (6) there is no injury to the test pieces by soaking or boiling.

General Principle.—Two vessels, A and B (Fig. 32) of volumes V and V_1 respectively are connected by a capillary tube and stopcock. Both are also

[1] Reference 13, p. 49–51, for exact procedure.

[2] References 14, 15, 16, 17.

provided with openings to the atmosphere closed by stopcocks. Vessel A holds the test pieces and is also provided with a manometer for measuring the pressure. Procedure: The weighed sample is placed in A and the pressure in A is reduced to P_0. Vessel B is closed off at atmospheric pressure. The stopcock connecting the two vessels is opened, and, when equilibrium is again attained, the second pressure P is read from the manometer. The per cent porosity is then

$$100\left(\frac{(B\text{-}P)V_1-(P\text{-}P_0)(V\text{-}V_B)}{(P\text{-}P_0)V_B}\right)$$

V_B is the bulk volume of the sample, which must be determined in another operation.[1] B in the formula is the outside or barometric pressure. The manometer can be attached to either of the vessels and the evacuation can be applied to vessel B if the proper change is made in the above formula. The above type of porosimeter has been used in the measurement of full-sized brick and other large samples in a quick porosity determination to note the degree of vitrification during the firing of the ware.[2]

Porosimeter for Highly Vitrified Wares.—A quick-acting porosimeter for highly vitrified bodies is described by Washburn (15) as the Washburn-Bunting porosimeter of the McLeod gage type. A cylindrical test-piece chamber, large enough to hold a 1- by 1- by 4-inch test piece is fitted with a large, ground-glass, hollow cap, which, after being constricted to a 5-millimeter internal diameter neck, expands above to a 100-cubic centimeter bulb, which in turn is terminated at the top with a graduated capillary tube and stopcock. At the bottom of the test-piece chamber is a stem to which is fastened a rubber tube and a 250-cubic centimeter mercury leveling bottle. The volume of air obtained from the pores of the test piece is measured in the graduated capillary tube at the top and compared with that from a reference test piece of the same size. Procedure: After the test piece is in place, the entire apparatus to above the stopcock is flooded with mercury from the leveling bottle and all the air removed except that in the pores of the test piece. By closing the stopcock and lowering the mercury level to below the test piece, a vacuum is established and the air emerges from the pores of the test piece. A second flood of mercury sweeps this air up into the capillary tube where it is measured. Refinements may be made by first removing the moist air from the apparatus and pores of the test piece and replacing it with dry air drawn in through a calcium chloride tube.

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Changes of Shape. *Warpage of Clays during Firing. Sagging.*—Warpage may be caused by three factors: (1) the continuation of drying warping or the relief of strains produced by irregular molding or drying, (2) the sagging from weight alone after vitrification or partial fusion has started, and (3) irregular firing shrinkage from the non-uniform application of heat. In the first and third cases the change of shape may be in a direction contrary to the

force of gravity. In the second, the sagging or slumping is due to the formation of a viscous silicate matrix which lubricates the unfused, granular skeleton. In others words, a second plastic state is developed; this time with viscous liquid films of glass surrounding unfused, granular particles. The rate of sagging closely parallels the rate of change in porosity and shrinkage during the early period of firing, but increases rapidly when the porosity and shrinkage have approached completion. Numerical correlation between warpage, shrinkage, and porosity cannot be closely made; each appears to be an independent, inherent property of each clay.[1] Tests were made by Beecher[2] to correlate warpage of fire clays with porosity, cone of fusion, and high-temperature softening under load. He found that, while general comparisons can be made, the amount of fluid portion of the clay and its viscosity change with increasing heat treatment is peculiar to each individual clay. The deformation under a compressive load of 25 pounds per square inch required in the specifications of the high-temperature load test should be comparable to the warpage of a heavy piece of fire-clay ware. But in the fusion of small cones, the viscosity of the fluid portion formed does not vary in direct proportion with the amount of fluid produced, and one cone may stand at a higher temperature than another because of the higher viscosity of its fused mass. When a load is applied, the differences due to viscosity become less, and any fluid material formed acts as a lubricant for the unfused skeleton. The state of distribution of a fluxing portion of the mass may cause differences in the warpage test which will not be indicated by the cone fusion test. For instance, if a flux covers only the surface of a mass of refractory grains and provides an internal lubrication for these grains, the brick will soften or deform under load at the softening point of the flux; but if the mass is pulverized for the cone fusion

[1] Worcester, W. G.: "The Warpage of Roofing Tile Clays," *Trans. Am. Ceram. Soc.*, **12,** 818 (1910).

[2] Beecher, M. F.: "An Investigation of Iowa Fire Clays," *Iowa State College, Eng. Exp. Sta., Bull.* 40, **14** (4), 62 (1915).

test, the intimate mixture of refractory grains and flux may soften under the very light load at an unexpectedly higher temperature. Flint fire-clay brick bonded with low-temperature plastic clays may give high cone fusion points and yet will soften under load at the softening point of the bond clay and not at the softening temperature of the arithmetical mixture of the two materials.[1]

Effect of Time on the Vitrification of Clays.—It has often been observed that the same degree of vitrification can be secured in burning clay wares by the application of heat at higher temperatures for a short time or at some lower temperature for a longer period. While 100° C. difference has been observed between the fusion temperatures of cones with rapid and slow heat treatment, this same relation will not hold with all compositions and for all temperatures. Calcareous clays, with their sudden development of fluid material, are more indifferent to the time effect than the feldspathic or siliceous bodies, which are very viscous at their melting points. It is not possible to cause a cone-10 procelain body to vitrify at cone 6 with any length of heat treatment.

Vitrification is dependent on the quantity and viscosity of the fluid material formed by the softening and interaction of the various silicates and fluxes. As the fluid material attacks the remaining skeleton, new mixtures of varying viscosity are formed, and the degree of vitrification is thereby altered. Regular dependence upon temperature and rate of heating can exist only when the amount of the softened material and its fluidity increase proportionally to the temperature increment.[2] Not only vitrification but also the vesicular structure is dependent on temperature and time. Both sound and poor structures can be

[1] ASHLEY, H. E.: "Method of Testing Sagger Mixes," *Trans. Am. Ceram. Soc.*, **12**, 277 (1910); tentative method for sag tests, 1921–1922, *Rept. Comm. on Standards, Am. Ceram. Soc. Year Book*, 27; WILSON, HEWITT: "High temperature Load Tests of Fire Brick," *J. Am. Ceram. Soc.*, **7**, 34–51 (1924).

[2] BROWN, G. H., and G. A. MURRAY: "The Function of Time in the Vitrification of Clays," *Trans. Am. Ceram. Soc.*, **15**, 193 (1913); *U. S. Bur. Standards, Tech. Paper* **17**.

produced at the same temperature with varying rates of firing.

Figure 33 gives the porosity-time-temperature curves of a Streator, Ill., paving brick shale.[1] Below 1100° C. the porosities are high and practically parallel to the abscissa. The rate of vitrification as shown by the drop in apparent porosity is very rapid at the beginning but slows up with further heating at the same temperature. The 1100 and 1150° curves if continued would apparently meet the 1200° curve after 1360 and 970 minutes respectively.

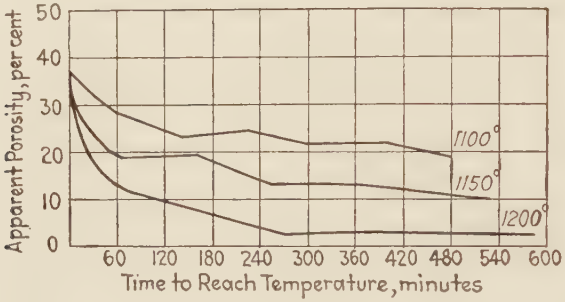


FIG. 33.—Effect of time and temperature on the porosity of a paving-brick shale from Streator, Ill. (*Bleininger, A. V., and T. L. Boys: Trans. Am. Ceram. Soc.*, **13**, 387 (1911).)

2. Chemical Action during Vitrification or the Effect of Certain Impurities on the Vitrification of Clays

Fluxes.—The term flux is a relative one and does not refer to a particular class of substances.[2] A flux is any material which will lower the softening, fusion, or liquefying temperature of another material. Bases act as fluxes to siliceous substances, while in basic compositions like portland cement, silica is a flux. Feldspar is a flux for whiteware mixtures and is regarded as a refractory material in

[1] BLEININGER, A. V., and T. L. BOYS: "The Function of Time in the Vitrification of a Shale," *Trans. Am. Ceram. Soc.*, **13**, 387 (1911).

[2] BLEININGER, A. V.: "The Influence of Some Fluxes and Non-fluxes on the Changes in Porosity and Specific Gravity of Clays," *Trans. Am. Ceram. Soc.*, **10**, 300 (1908).

the low-temperature metal enamels.[1] With silicates, a small portion of any substance, dissolved in another, will lower the fusing point, provided no chemical reaction takes place. Nevertheless, with ceramic materials, the fluxes can be separated into two classes: (1) those like lead oxide, the alkalies and borates,[2] which melt at very low temperatures, and feldspar at higher temperatures, to provide a liquid into which the more refractory portions gradually dissolve; and (2) those fluxes like lime, magnesia, zinc and barium oxides, which are very refractory materials alone, but by eutectic combinations produce glasses of much lower softening points. The former are not so dependent on eutectic action because of their own low melting points, but even these can be reduced by the addition of other substances.

Action of Feldspar.—The feldspars form the chief source of the alkalies and some of the lime found in clays. Most of the feldspars on the market for use in whiteware bodies and glazes are mixtures of the potash, with the soda and even small quantities of the lime feldspar (anorthite). The potash feldspar, microcline (orthoclase), is preferred for body work requiring a high degree of vitrification, as it has the reputation of a longer and safer temperature range. For glaze work, the albite and even the plagioclase give good results if the minimum temperature of fusion is desired. In Simonis' work (Fig. 81) pure feldspar is shown to have the lowest deformation point of any mixture of kaolin, flint, and feldspar, so that any eutectic action of either the kaolin or flint on feldspar must lie very close to that of pure feldspar. Although the softening point of the average commercial potash feldspar is in the neighborhood of cone 8, yet it begins to interact with the clay material at a much lower temperature. Berdel found that the dissolving action of potash feldspar begins as low as cone 09. Bleininger and Moore (1)[3] found that a potash

[1] STALEY, H. F.: "Materials and Methods Used in the Manufacture of Enameled Cast-iron Wares," *U. S. Bur. Standards, Tech. Paper* 142, 7 (1919).

[2] An eutectic action is noticeable even with these materials.

[3] See reference 1, p. 194.

feldspar showed solution effects with kaolin as low as cone 06. Cornish stone, a mixed feldspar from Cornwall, England, widely used in this country, gives even slower neutral fluxing effects than feldspar and is a safer flux when range and rate of vitrification are considered.

a. The Melting of Potash Feldspar(2).[1]—Potash feldspar (orthoclase) melts incongruently at 1170° C., breaking up into liquid and leucite, $K_2OAl_2O_34SiO_2$ (see Fig. 72). The leucite disappears at 1530° C. after a melting interval of 360°. The other three natural potash feldspars, microcline, sanidine, and adularia, show the same kind of behavior. Slivers of feldspar crystals when placed on end in a cone fusion furnace do not melt like crystalline compounds of definite melting points, but bend like pyrometric cones or show the gradual deformation of amorphous clays. This is probably caused as much by the high viscosity of the fluid formed above the melting point as by the fact that it melts incongruently.

b. The Plagioclase Feldspars.—Albite and anorthite form a continuous series of solid solutions, the melting points of which change in almost a linear relation to the percentage composition of the two silicates(3), or, in other words, the triclinic feldspars form an isomorphous series. It has been difficult to determine the exact melting point of albite because of the extreme viscosity of the melts and also because the presence of but 2 per cent anorthite is sufficient to cause a melting interval of about 50° C. (4) (see Fig. 44 for melting points).

c. Soda versus Potash Feldspar.[2]—It is believed that the reason why soda feldspar is not in more common use in the ceramic industry is because, the quantity of soda feldspar being small in comparison with the present abundance of potash feldspar, experimental data and plant research work have not been done to develop soda feldspar bodies and glazes. With the exception of the French porcelains,

[1] See reference 2, p. 194.

[2] Wilson, Hewitt: "Feldspars of the Pacific Northwest," *U. S. Bur. Mines, Rept. of Investigation* No. 2794 (1927).

it appears that the Europeans are not acquainted with soda feldspar. A. S. Watts(12), one of the authorities on feldspar, is about the only experimenter with published data who has made comparisons of the two varieties in porcelain bodies. He found practically no difference in the degree of vitrification, warpage, and quenching resistance when soda feldspar was substituted for potash feldspar, but did find a difference in the tone of the vitrified ware when tested for "ring" or pitch. The soda-feldspar body had the higher pitch. Watts(12) states, however,

> Since a soda-feldspar porcelain is to all appearances equal in all the above properties to the potash porcelain, it appears to me to offer a means of cheapening the cost of many bodies where this particular quality of sound does not represent any value.

In later work, Watts(13) also found that mixtures of soda and potash feldspars soften or deform before the soda feldspar itself when heated in the cone shape, and that mixtures of the two feldspars cause greater warpage and shrinkage in porcelain bodies, but that the *soda feldspar alone does not cause this trouble*(14). On the other hand, the translucency increases with soda feldspar up to cone 8. It is believed by the author that soda feldspar is a more active flux(15) than the potash feldspar and is active at a lower temperature, but that the temperature-vitrification range is nearly as long as that of potash feldspar. Staley(16) found that potash gives more brilliant glasses than soda, but nevertheless the soda glasses are more resistant to chemical agencies. Otherwise they appear to be interchangeable in metal enamels with slight variations in the batch composition. Flint(17) in writing specifications for feldspar to be used in glass manufacture makes no distinction between the potash and soda varieties, stating that "the most important consideration in the use of feldspar is that the total alkali be constant and high enough to warrant its use," otherwise more soda ash must be added.

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The Action of Lime.—The effect of lime on the vitrification of clays is variable and irregular when compared to that of feldspar or Cornish stone. Alone, it is very refractory (melting point 2572° C.) and in clays its presence is not noticed save as a refractory until the eutectic temperature is reached. Then a very fluid glass is suddenly formed, which reduces the vitrification range of the clay body.[1]

[1] Rieke: *Sprechsaal*, **40,** Nos. 44, 45, 46; *Cramer. Tonind.-Ztg.*, 197 (1887), and 73 (1888).

Lime also forms a number of compounds with alumina and silica, and this action tends to give an irregular fluxing effect with different amounts of CaO. With some clays or shales, the lime will first act as a refractory substance before the fluxing temperature is reached. With high

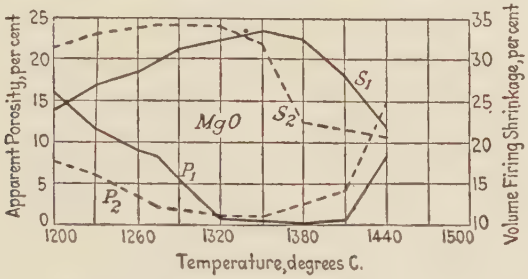


FIG. 34.—Effect of MgO on the vitrification of a porcelain body.

alumina clays, very little fluxing effect is noted below cone 2. In ferruginous shales containing less than 1 per cent CaO, the maximum fluxing effect is shown by the addition of not more than 5 per cent of the carbonate.[1] Lime is an undesirable constituent in a paving-brick shale, not only

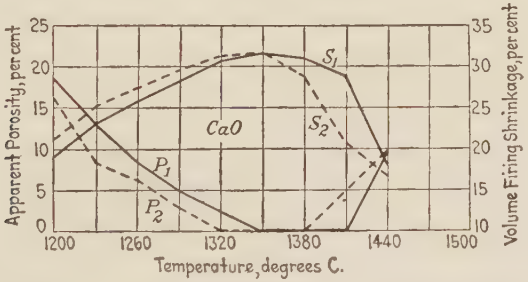


FIG. 35.—Effect of CaO on the vitrification of a porcelain body. S_1 and P_1 bodies contain 0.2 per cent MgO and CaO, respectively, while S_2 and P_2 bodies contain 1.0 per cent of these fluxes. (*Riddle, F. H., and W. W. McDanel: J. Am. Ceram. Soc.*, **1**, 622 (1918).)

because of its sudden flux effect but also because of its tendency to produce vesicular structure. Lime does not hasten the maturing of porcelain bodies but causes over-

[1] BLEININGER, A. V.: "The Influence of Fluxes and Non-fluxes on the Changes in Porosity and Specific Gravity of Clay," *Trans. Am. Ceram. Soc.*, **10**, 324 (1908).

burning at a lower temperature and shortens the firing range considerably[1] (Fig. 35).

Powdered limestone is dusted on the plastic-brick columns as they emerge from the auger-machine die in the Chicago common-brick yards to prevent sticking in the kiln. The surface glacial clay already contains considerable limestone as pebbles, and the CaO here no doubt acts as a refractory substance. The color is bleached to a dirty buff. If the limestone is present within the brick as pebbles, the expansion upon carbonation and hydration after firing often disrupts the structure. A direct change form CaO to $CaCO_3$ (dry atmosphere) is apparently worse than the change from CaO to $Ca(OH)_2$ and then to $CaCO_3$.

Action of Magnesia.—Magnesia is considered to be a less dangerous flux than lime, for it exerts less fluxing action, acts as a flux through a shorter range of per cent additions, and does not produce the fluidity of lime. As the amount of magnesia increases in a clay body, it more quickly assumes refractory properties and retards rather than accelerates vitrification and fusion. Less than 1 per cent of MgO was beneficial in lowering the firing temperature of porcelain bodies, causing them to mature, but likewise to overfire at lower temperatures[1] (Fig. 34). Impurities of lime in magnesia refractories cause a lowering of the temperature at which failure under load will take place and easier disintegration due to the fluxing action of slags or outside silicate combinations.

Action of Iron Oxide.—Very little work has been done by ceramists on the fluxing power of ferric oxide, because it it is a deleterious impurity in the synthetic whiteware bodies, and the red-burning clay combinations are still too complex for ready study. As shown in Chap. VI, p. 162, ferric oxide is reduced to Fe_3O_4 above 1300° C. even under oxidizing conditions. Hence, the iron is reduced by the original

[1] Riddle, F. H., and W. W. McDanel: "Some Types of Porcelain," *J. Am. Ceram. Soc.*, **1**, 606–627 (1918).

firing of fire brick and should be considered as a ferrous silicate in subsequent furnace service.

Hofman(1) gives the following softening temperatures for various ferrous silicates:

Compound	Temperature, degrees Centigrade	Compound	Temperature, degrees Centigrade
$4FeOSiO_2$	1280	$3FeO2SiO_2$	1140
$3FeOSiO_2$	1220	$4FeO3SiO_2$	1120
$2FeOSiO_2$	1270	$FeOSiO_2$	1110

Rieke (2)[1] found an eutectic at cone 3 between FeO and $Al_2O_32SiO_2$ at two molecules of the FeO to one of the aluminum silicate. These low temperatures would indicate that the ferrous oxide is a very active flux. The coloring power of iron is strong, and badly discolored clay, or silica brick, will often give a high fusion point. Iron oxide is the best-known high-temperature bonding material for refractory magnesia brick, as magnesioferrite, $MgOFe_2O_3$, aids in the development of a rigid structure with periclase. Lime and silica on the other hand produce low-fusing silicate mixtures which soften at lower temperatures. When FeO is in combination with Cr_2O_3 to form the spinel, chromite, $FeOCr_2O_3$, a very refractory compound is found.

Ferric oxide is not a very effective flux when added to kaolins or ferruginous clays(4)(5). Kuechler(3) found that about 10 per cent Fe_2O_3 lowered the deformation point of a Florida kaolin about six cones, and its fluxing power was similar in the deformation test to that of TiO_2. Ferric oxide combines more rapidly with siliceous clays than with the high aluminous materials. An excess of iron oxide tends to promote a vesicular structure at the higher temperatures due not only to the release of oxygen while changing from the ferric to the ferrous forms but also to the vaporization of the iron oxide itself.

Sheerar(6) found that the addition of iron pyrites to a fire clay gave noticeably inferior high-temperature load-test results. An increase in iron content caused a greater

[1] See reference 2, page 198.

expansion in the initial heating period and a contraction at lower temperatures during the slumping period. A reducing atmosphere magnified the effect of the iron. High-iron fire clays are noticeably affected by reducing atmospheres in metallurgical furnaces(7).

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3. Reversible Thermal Expansion of Clays[1]

Kaolin and bauxitic fire clay have a regular reversible expansion after firing which varies but little with the original temperature of firing. Fire clays and other clay mixtures containing free quartz after being fired to cone 9 or below show a large expansion between 500 and 600° C. but when fired to higher temperatures, cones 14 or 20, gradually lose this peculiarity due to the destruction of the quartz by its interaction with the clay material and fluxes. This interaction takes place more readily with fine-grained, fusible clays and is retarded if the quartz is coarse grained. Amorphous silica shows a large expansion between 100 and 250° owing to the supposed formation of cristobalite.

[1] Houldsworth, H. S., and J. C. Cobb: "Reversible Thermal Expansion of Fire Clay and Other Refractory Material," *J. Soc. Glass Tech.*, **5** (17), 16 (1921).

When the amorphous, precipitated silica is mixed intimately with kaolin and a little soda, however, regular expansion after calcination to cone 06 or cone 9 is found. Increase in porosity up to 50 per cent is accompanied by a decrease in expansion. Magnesia brick, carborundum, or alumina bonded with 10 per cent ball clay show no irregularites.

When quartz particles are embedded in a mass of soft and comparatively porous, fired kaolin, the loss in compressive strength on quick reheating is very low in comparison with those bodies in which the quartz is embedded in a tight and vitrified-clay mass. The kaolin body has more ability to "give and take," while the vitrified body is shattered by the quartz volume changes.[1]

[1] Goodrich, H. R.: "Spalling and Loss in Compressive Strength of Fire Clay Brick," *J. Am. Ceram. Soc.*, **10** (1927).

CHAPTER VII

MELTING, FUSION, AND CRYSTALLIZATION OF SILICATES

A. CRYSTALLINE CERAMIC BODIES

Raw and dried clay is largely composed of colloidal and amorphous material. High temperatures tend to eliminate the colloidal phases and to replace them with the corresponding silicate glasses, together with small amounts of the more easily and quickly formed crystalline mullite which has been found in low-temperature paving brick and high-temperature porcelain bodies. Although as in china-ware bodies, the crystalline material such as feldspar and quartz may amount to 50 per cent of the composition, yet but little of this is obtained as crystalline matter after heating, because the rate of cooling in ceramic furnaces and kilns is too fast for the crystalline growth of most silicates. The ceramic industry as a whole is primarily interested in the production of amorphous materials. The structural pottery industries wish to produce ceramic bodies which are hard and strong, that is, with a large content of glass bond, but which have sufficient rigidity at the maximum temperature of the kiln to resist deformation or loss of shape. On the other hand, these viscous bodies afford very little opportunity for the development of crystals, and mullite appears to be the only one active enough to develop in the ordinary clay mixture.

At present, however, interest is being displayed in those crystalline forms which are useful in refractory work because of their rigidity under pressure at temperatures close to their melting points and because of the greater inertness of crystalline materials to the action of active agents such as slags and glasses. The electrical-insulator

industry has recently introduced a high content of mullite into spark-plug bodies because of the better resistance to a combination of electrical and thermal stresses. The Corning Glass Company[1] and others are engaged in commercial experiments of a revolutionary character. Mullite is melted in an electric furnace and cast directly in sand molds to produce glass tank shapes. These are carefully annealed to prevent strain and thus produce a solid mass of interlocking crystals, with the maximum resistance to load and slag or glass action at high temperatures. Heretofore, mullite, corundum, and other crystalline masses have been crushed, bonded with plastic fire clays, milk of lime, etc., and refired in ordinary combustion kilns. In some cases, as in silica and special mullite brick, a second interlocking crystallization could be produced. In most cases, however, the bond was amorphous and the character of the product very largely depended on this bond. Recrystallized silicon carbide refractory products have been on the market for many years. The second growth of crystals is produced in electric resistance furnaces without a silicate bond. Silicon carbide has no melting point but rather a dissociation temperature at 2240° C.

Other crystalline ceramic forms include corundum, Al_2O_3, in aluminous bauxite and diaspor, calcium silicates and aluminates in different cements, periclase in magnesia brick, and spinel, $MgO.Al_2O_3$, in the "Diamel" brick of the Vitrefrax Company. In selecting such high-temperature refractories for casting wares, it is necessary to obtain fluidity with comparatively low vapor pressure over a workable temperature range, together with rapid crystallization. Magnesia and lime vaporize very fast, and, while quartz melts at comparatively low temperatures, it crystallizes too slowly from its melt. Fused silica finds its best service in the production of amorphous silica glass wares. With the recent rapid commercial development of the electric furnace, we will soon have more data on the behavior of

[1] ANONYMOUS: "Tank Block Problem Solved at Corning," *Glass Ind.*, **7**, 257 (1926).

these high-temperature compounds. The delayed solution of the lime problem may be found in the production of some high-temperature compound of this cheap, abundant, very refractory, but as yet, far too unstable and active material for high-temperature service.

B. GENERAL DEFINITIONS

1. Crystalline Substances

Crystals are bodies having a definite geometrical arrangement of their molecules, and under favorable conditions of free space, time, and surroundings will be bounded by plane surfaces at definite angles to each other and characteristic of the substance.[1] With the exception of crystals belonging to the isometric and cubic systems, crystals show a constancy of properties in parallel directions and varying properties in directions not parallel[2] (anisotropic bodies). A mass of crystalline material may not show the outward appearance of crystalline structure because of the simultaneous growth and interference of crystals in a limited space (for example, large masses of vein quartz). In cryptocrystalline or microcrystalline structures, the crystals are of microscopic or submicroscopic size.

2. Solids

Solids are bodies which possess rigidity or offer resistance to deformation by mechanical force.[3] While solidity is more common to crystalline substances than to liquids, some crystals do not possess rigidity and some liquids do to a very pronounced degree. Tammann and Mehl state that no theoretical, qualitative distinction exists between the solid and the liquid state.[4] Liquids have relatively low viscosity, which indicates that their molecules are easily displaced. The molecules of even crystalline solids, how-

[1] Moses and Parsons: "Elements of Mineralogy."

[2] Washburn, E. W.: "Principles of Physical Chemistry," p. 65 (1915).

[3] Maxwell, J. C.: *Sci. Papers*, **2**, 620, Cambridge (1890).

[4] Tammann, G., and R. F. Mehl: "States of Aggregation," p. 283, D. Van Nostrand Company (1925).

ever, possess the same property, especially at temperatures close to the melting point, as is shown by the hot working of metals and the behavior of ice in glaciers.

3. Melting

The atoms or molecules of a solid are confined to short periods of vibrations about definite position of rest while those of a liquid are more or less freely movable. As a solid is heated, the amplitude of vibration increases until the atoms approach and influence each other so strongly that some no longer return to their original positions. A definite temperature is finally reached where so few atoms return that the structure of the crystal is destroyed or the crystal is said to melt. *The congruent melting temperature is the constant temperature at which the liquid and crystalline phases of the same composition are in equilibrium with each other.* Melting does not always mean fluidity, for a crystalline solid may change to an amorphous solid. A crystalline solid is said to melt incongruently when at a definite temperature it changes to another crystalline composition and a liquid.

4. Crystallization[1]

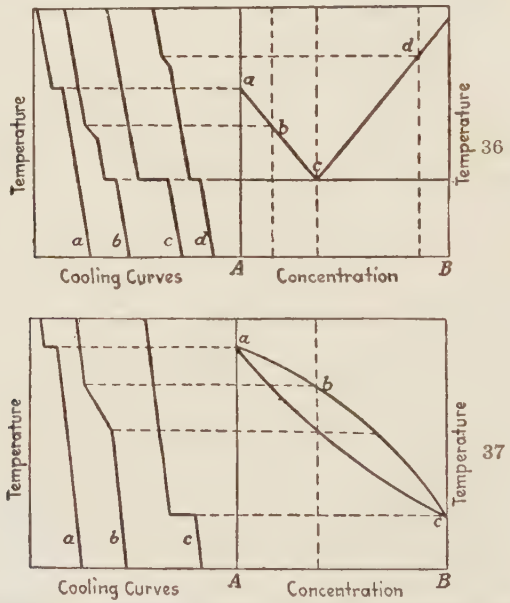
From the above description of melting, it is apparent that solids cannot be superheated above the melting temperatures. The formation of a solid crystal from the liquid is a more difficult process with silicates than the destruction of the crystalline structure. Crystallization is retarded by the molecular complexity of the crystal and the viscosity of the liquid at the crystal-forming temperatures. The formation of a crystal requires certain definite arrangements and adjustments of the molecules in the liquid. The greater the number of molecules required and the greater the viscosity or the retarding action of the liquid to movement, the more difficulty will be experienced in obtaining crystallization. Most pure metals and some salts like

[1] Eucken, A., E. R. Jette, and V. K. LaMer: "Fundamentals of Physical Chemistry," pp. 177, 198, McGraw-Hill Book Company, Inc. (1925).

NaCl build simple crystals of atoms instead of molecules, and hence crystallization proceeds very rapidly. With complex molecules, such as the silicates, crystallization is handicapped by high viscosity of the liquid and usually starts from small nuclei or crystallization centers which direct the neighboring liquid molecules to the proper arrangement. The velocity of crystallization or the rate of growth of a crystal is likewise dependent on the rate at which the heat developed by crystallization is conducted away.

5. Supercooled Liquids and Amorphous Solids

As a liquid is cooled, the viscosity increases. With some liquids, the viscosity at the freezing point is so great



Figs. 36 and 37.—Comparison between cooling curves and temperature-concentration diagrams. A simple eutectic system is shown in Fig. 36 and a simple isomorphous series in Fig. 37.

that the molecular motion within the liquid is decreased to the point of preventing crystalline growth. In this case, the liquid is supercooled until it becomes a rigid glass.

No crystalline phase has appeared and the rigid liquid is called an *amorphous solid* to distinguish it from crystalline solids which have both a definite melting point and a definite crystalline structure. On heating, amorphous solids gradually soften until they become quite fluid, but no one temperature is found above which they may be called liquid and below, solid. Sometimes rigid glass will slowly crystallize. This change is called *devitrification.*

Amorphous solids may not only be supercooled liquids possessing a glassy or vitreous structure, but also may be formed by chemical action, such as the chemical disintegration of crystalline rocks to form amorphous clay. Amorphous substances may possess the *glassy, colloidal,* or *cellular* structure. It is difficult to distinguish between the truly amorphous and the cryptocrystalline structure.

6. Polymorphism, Transition, Inversion

Polymorphism is the property of a substance to exist in more than one crystalline form. The transition from one form to another is usually accompanied by a pronounced change in volume and an appreciable evolution or absorption of heat. It also occurs at a definite temperature called the transition or inversion point, and this temperature is the only one at which the two distinct crystalline phases are in equilibrium with each other.[1] At 870° C. quartz and tridymite are in equilibrium with each other. Above 870° tridymite is the stable form and below this temperature quartz alone is stable. In the case of quartz and most silicates, the molecular motion within the crystalline structure is very slow and both phases can often be kept at ordinary temperatures for long periods of time, although only one form is stable and a tendency exists in the unstable form to change over. Both of the crystalline modifications

[1] Ferguson, J. B.: "The Term Inversion," *Science,* N.S., **50** (1302), 544–546 (1919).

Note.—The variable inversion temperature of cristobalite (Fig. 38) is a phenomenon of *unstable equilibrium.*

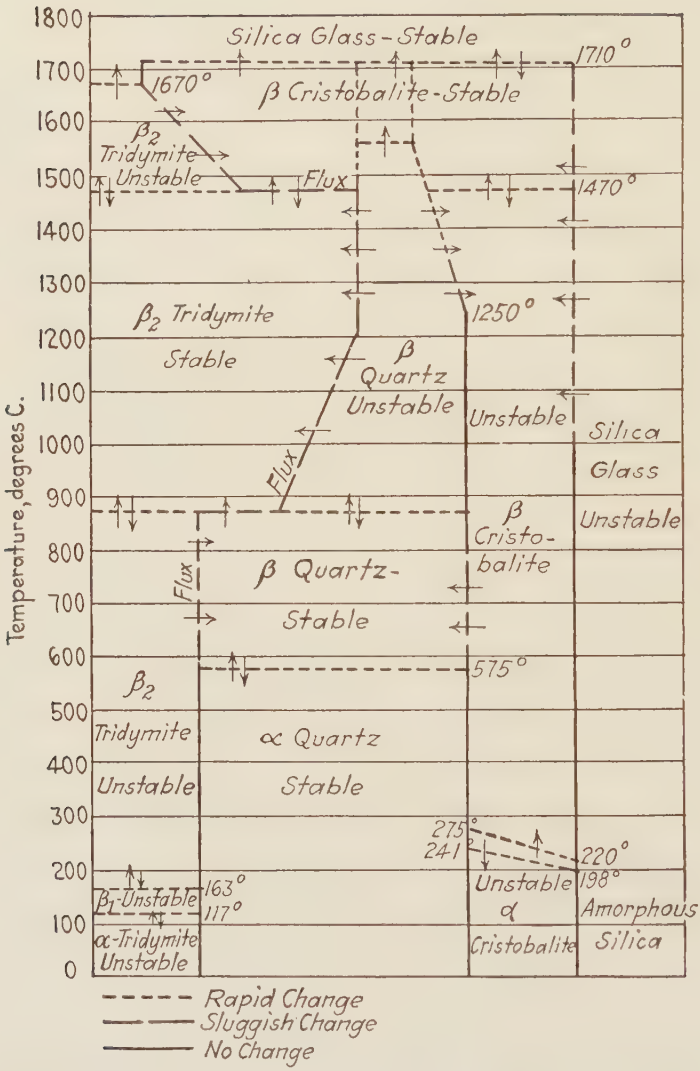


FIG. 38.—Stability relations of the silica minerals. This diagram is a revision of that made by J. Spotts McDowell. (*Trans. Am. Inst. Mining Eng.*, 2003 (1917).)

of calcium carbonate, calcite, and aragonite are found in nature, although only the former is stable.[1]

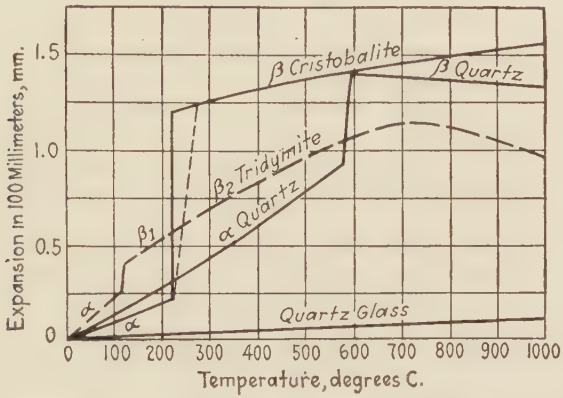


FIG. 39.—Thermal expansion of silica minerals. (*LeChatelier: "La Silice," Revue Universelle des Mines* (5), **1**, 90 (1913).)

Examples: quartz (sp. gr. 2.65) inverts to tridymite (sp. gr. 2.27) at 870° and the latter to cristobalite (sp. gr.

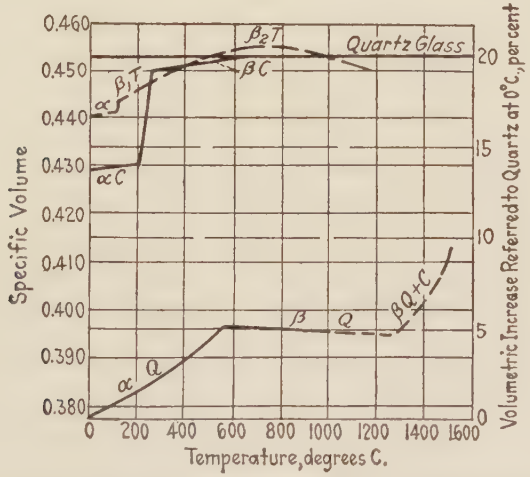


FIG. 40.—Thermal expansion of silica minerals. (*Day, Sosman, and Hostetter: Am. J. Sci.* (4), **37**, 1–39 (1914).)

2.34) at 1470° (see Figs. 38, 39, and 40). Similar inversions are known for calcium meta- and orthosilicate. Thus

[1] WASHBURN, E. W.: "The Principles of Physical Chemistry," pp. 66, 67 (1915).

we have the pseudo-metasilicate and wollastonite and likewise three forms of calcium orthosilicate. These are the alpha, beta, and gamma modifications, whose densities are 3.27, 4.28, and 2.97, respectively.

7. Isomorphism, Solid Solution, and Mixed Crystals

The word "isomorphism" etymologically refers to crystals which are alike in shape and thus when formed together can produce crystals containing both substances. Some confusion has arisen in the use of the term, owing to the fact that some substances possessing identical crystalline shapes are not miscible in the solid state. Equal valencies, chemical relationship, and crystalline similarity alone are not sufficient to determine miscibility in the solid state for the fundamental crystalline structures must not only be alike in shape but also the molecular volumes of the two substances must be nearly equal.[1]

The term "solid solution" should be confined to mixtures of substances which are miscible in all proportions, or in other words an intermingling of molecules. The term can thus be applied to cases of complete crystalline miscibility such as that of albite and anorthite (crystalline solid solution) or to glasses (amorphous solid solution). It would be better to apply the term *mixed crystals* only to such mixtures in which the separate crystals can be identified. Some crystals can be replaced by others to only a limited extent, that is, they form some crystalline solid solution, but an excess of either produces mixed crystals. Examples, potash and soda feldspars.

In Fig. 44 (concentration-temperature diagram of anorthite and albite mixtures), the two-phase system consists of two solutions, each represented by a curve showing the liquid and solid solutions in equilibrium with each other at the different temperatures. The field above the upper

[1] Bowen, N. L.: "Melting Phenomena of the Plagioclase Feldpsars," *Am. J. Sci.*, **35**, 595 (1913).

Wherry, E. T.: *Am. Mineral.*, **8**, 1–8 (1923).

or *liquidus curve* represents liquid solutions and that below the lower or *solidus curve* represents solid solutions.

C. CHANGE IN MOLECULAR VOLUME DURING MELTING

The molecular volume of most silicates increases on deformation and the density decreases (see Fig. 29). The molecules of an amorphous solid have only a heterogeneous arrangement, but this state represents a greater energy potential than does the crystalline state. The amorphous modifications are usually more soluble and capable of quicker reactions.[1]

TABLE XXIII.—SPECIFIC GRAVITY CHANGES OF SILICATES WHEN MELTED[1]

	Specific gravity crystal	Specific gravity glass	Per cent reduction
Mica	3.07	2.24	27.0
Quartz	2.66	2.23	16.3
Olivine	3.38	2.86	15.6
Sanidine	2.58	2.38	7.6
Orthoclase	2.57	2.32	9.6
Albite	2.60	2.04	21.9
Oligoclase	2.66	2.26	15.1
Labradorite	2.73	2.57	6.1
Hornblende	3.22	2.83	12.2
Augite	3.27	2.81	14.2
Granite	2.68	2.43	12.9
Gabbro	3.10	2.67	14.2

[1] ROTH: "*Allegemeine and Chemishe Geologie*," **11,** 52; PURDY, R. C.: "Paving Brick and Paving Brick Clays," *Illinois Geol. Survey, Bull.* 9, 251 (1908).

D. HEAT OF MELTING OF SILICATES

The factors involved in the relative ease of liquefying a substance are (1) the melting point, (2) the quantity of heat which it absorbs in melting, that is, its heat of melting, and (3) its thermal conductivity. If one material has a much higher heat of melting than a second, it may be pos-

[1] BLEININGER, A. V., and J. K. MOORE: "The Influence of Fluxes and Non-fluxes upon the Change in Porosity and Specific Gravity of Some Clays," *Trans. Am. Ceram. Soc.*, **10,** 294 (1908).

sible to melt the second more easily even if the former's melting point is lower.

TABLE XXIV.—HEATS OF MELTING OF SOME SILICATES[1]

Substance	Melting point	Molecular weight	Heat of fusion per gram	Heat of fusion per mole	Observer
Anorthite, $CaOAl_2O_32SiO_2$	1550°C	279	100	28,000	Vogt
Diopside, $CaOMgO2SiO_2$	1225	217	100	22,000	Vogt, White
Enstatite, $MgOSiO_2$	1375	201	125	25,000	Vogt
Olivine, $2MgOSiO_2$	1890	141	130	18,000	Vogt
CaO	2570	56.1	490	30,000	Washburn (calculated)
MgO	2800	40.3	700	30,000	Washburn (calculated)

[1] WASHBURN, E. W.: "Latent Heats of Fusion of Lime and Magnesia," *Trans. Am. Ceram. Soc.*, **19**, 199 (1917).

E. EUTECTIC ACTION

Melting Eutectics.—When one compound is added to another in increasing amounts, the melting temperatures of the mixtures are successively lowered until a composition is reached, called the "eutectic composition" which has the lowest melting temperature of the system. The "eutectic point" is the temperature at which a solution having the eutectic composition is in equilibrium with both crystalline phases at the same time.

On heating any composition *d* (Fig. 41–1) between that of the eutectic and one of the components *A* to the eutectic temperature, the maximum amount of material of eutectic composition will melt. Further rise of temperature causes more of the component *A* to be taken into solution until the melting temperature of *d* is reached. All of the second component present in *d* is melted at the eutectic temperature. The composition of the melted portion of the mass therefore changes from that of the eutectic to that of the mixture *d* or the amount of *A* gradually increases in the melted portion as the temperature rises. The softening point usually lies

between the eutectic and the final temperature of melting, the distance above the eutectic temperature varying inversely with the amount of the eutectic composition present in the mixture and also upon the viscosity of the fluid formed.

On cooling from a melted condition, the reverse takes place. When the temperature drops to the liquidus point of *d*, the solid portion first formed has a composition of the component *A*. Below this temperature to that of the eutectic, the melted portion throws out more of *A* until all becomes solid at the eutectic. With mixtures of three components the diagrams can become very complicated.

The temperatures on the liquidus curve (omitting, of course, those of the eutectic and the two components) should not be called "melting temperatures," but rather "saturation temperatures,"[1] The crystal form which appears has been precipitated from solution and is not of the same composition as that of the liquid from which it came. Stable compounds and stable quintuple or quadruple points[2] are the only bodies which have true melting points or temperatures at which the solid is in equilibrium with a liquid of its own composition.

F. TEMPERATURE-CONCENTRATION DIAGRAMS[3] (PHASE RULE)

1. General Theory

The Application of the Phase Rule of Willard Gibbs to Silicate Mixtures.[4]—A *phase* is a homogeneous, physically distinct, and mechanically separable portion (solid, liquid,

[1] Feild, A. L., and P. H. Royster: "Temperature-viscosity Relations in the Ternary System CaO-Al_2O_3-SiO_2," *U. S. Bur. Mines, Tech. Paper* 189 (1918).

[2] See Chap. VII, p. 214, typical three component systems, case 1.

[3] Entire credit is given for the theory of these temperature-concentration diagrams and the remarkable development of the diagrams themselves to the members of the Geophysical Laboratory, Carnegie Institute of Washington. The following typical systems are given by G. A. Rankin and F. E. Wright (*Am. J. Sci.*, **39**, 17–19 (1915)).

[4] Findlay: "The Phase Rule," pp. 8, 9, 12, Longmans, Green & Co., London (1923).

or gas) of a heterogeneous system. The *components* of the heterogeneous system are "the smallest number of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation(1)." The number of *variable factors* or *degrees of freedom* of the components are the temperature, pressure, and concentration, "which must be arbitrarily fixed in order that the condition of the system may be perfectly defined." The phase rule expresses the relationship between the number of phases (P), the degrees of freedom (F), and the number of components (C) which are in equilibrium as follows:

$$F = C + 2 - P$$

The rules for the application of the phase rule in silicate equilibria without solid solution would be:

1. The vapor pressures are unimportant for most of the temperatures studied. This leaves but two degrees of freedom—temperature and concentration.
2. The vapor phase must always be considered as present.
3. The liquids are miscible in all proportions and hence only one liquid phase occurs.

Non-variant Systems.—If the magnitudes of C and P are such that F is equal to zero, the system is *non-variant.* Such is the case of the eutectic composition at its melting point. In a two-component system equilibrium is established between two components, two solid phases, one liquid phase, and one gaseous phase.

$$F = 2 + 2 - 4 = 0$$

If the system is non-variant, nothing can be disturbed without destroying the equilibrium. Only one temperature and one composition or concentration can be found with these four phases in equilibrium. The melting point in a one-component system also represents a non-variant system.

Univariant Systems.—F may equal unity with one solid, one liquid, and one vapor phase in equilibrium, which

condition exists at the saturation temperature of any composition between the eutectic composition and either component in a two-component system. In other words, either the composition or the temperature can be changed within limits without causing a phase to disappear. But both cannot be changed independently at the same time. With different temperatures, solid A can exist in equilibrium with a liquid, composed of A and B, but the composition of this liquid must vary to meet the requirements of the temperature change. The boundary lines of a three-component system also represent univariant systems.

$$F = 3 + 2 - 4 = 1$$

Bivariant System.—The boundary fields themselves in a three-component (triaxial diagram) system represent bivariant systems, where one solid phase is in equilibrium with liquid and vapor phases:

$$F = 3 + 2 - 3 = 2$$

Non-variant systems are represented by fixed points. If any change is made, the location is disturbed. Univariant systems are represented by lines, bivarent systems by areas and fields. A point may be fixed on a line of a coordinate diagram by locating a single coordinate.

Typical Two-component Systems (Fig. 41).—Case 1 is the simple eutectic system between components A and B. Example: CaO-MgO system.

Case 2 shows the formation of a compound AB, which is stable at low temperatures but breaks down at t into the two solid components, which react as in Case 1 at the higher temperature. Examples: the disintegration of $3CaOSiO_2$ in the system, $CaO\text{-}2CaOSiO_2$; sillimanite or kaolinite in the $Al_2O_3\text{-}SiO_2$ system.

Case 3 shows that the compound AB does not break down until above the eutectic temperature and is thus able to make its appearance on the liquidus curve. AB, however, has an incongruent melting point and is replaced by solid B and a liquid. Example, mullite in the $Al_2O_3\text{-}SiO_2$ system.

In Case 4 the compound AB has a definite congruent melting point and the system is divided into two simple independent eutectic systems A-AB and AB-B.

Case 5 represents continuous isomorphous mixtures of A and B with no minimum temperature. Example, the plagioclase feldspars, albite and anorthite.

Case 6 represents isomorphous mixtures of A and B with a minimum temperature. Example, the system gehlenite-akermanite (Fig. 45).

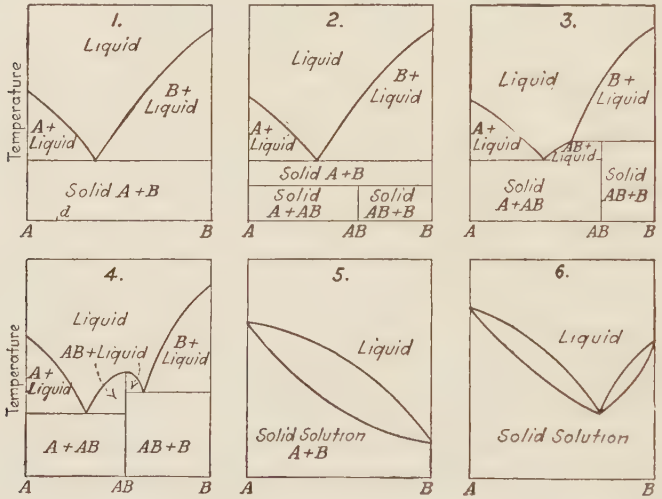


FIG. 41.—Six types of concentration-temperature diagrams for binary systems.

Typical Three-component Systems (Ternary Diagrams) (Fig. 42).—The three-component systems are but combinations of two component or binary systems.

Case 1.—This is an extension of three simple eutectic diagrams to cover all possible mixtures of three components. *Boundary lines* (saturation curves) separating the three fields of A, B, and C connect each binary eutectic with the ternary eutectic near the center. As the liquidus line of a binary system between that of a component and the eutectic represented the series of temperatures and liquid compositions from which that component separated, so the area or field adjacent to each of the three components repre-

sents all possible compositions of liquid in which that component is the first crystalline or primary phase to appear. Or one crystalline phase is in equilibrium with a liquid and vapor:

$$F = 3 + 2 - 3 = 2 \text{ (bivariant)}$$

The boundary lines represent two crystalline phases, those of the two adjoining fields, in equilibrium with liquid and vapor. Being a line, it is a univariant or monovariant

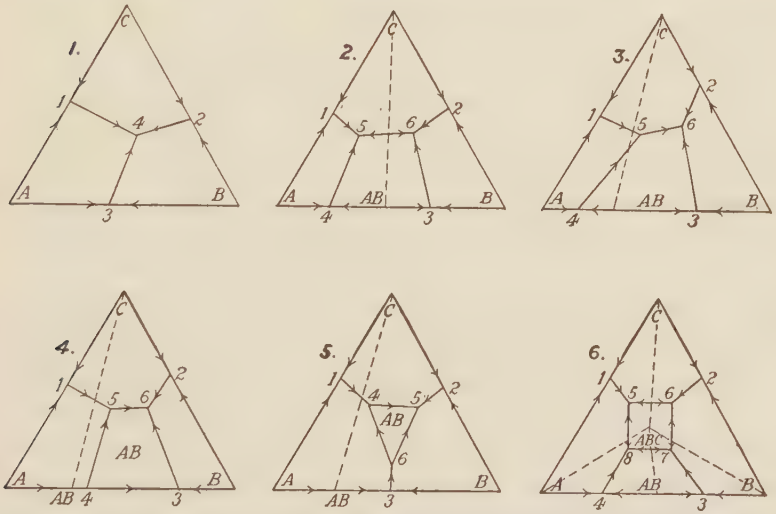


FIG. 42.—Six types of concentration-temperature diagrams for ternary systems. (*Rankin, G. A., and F. E. Wright: Am. J. Sci.*, **39**, 18 (1915).)

equilibrium. The ternary eutectic is non-variant. The binary eutectics have four phases in equilibrium and are called "*quadruple points.*" The ternary eutectic has five phases in equilibrium and is called a "*quintuple point.*" A more recent method eliminates the vapor phase or holds the pressure constant and expresses it as a "*quadruple* (*P*) point."

The temperatures can be represented only on a triaxial diagram by separate isotherm lines or by a space diagram built up in three dimensions in which the vertical distances to the surface represent the temperatures. The tempera-

tures always fall as they leave the boundary towards the interior of the triangle, though they may rise in other cases in the interior.[1]

Case 2.—The third binary system in this triaxial is that of the fourth case of the binary systems. The compound AB, stable at all temperatures up to its melting point, divides the diagram into two simple ternary diagrams, A-C-AB and B-C-AB. The dotted line C-AB is called a "conjugation line" and represents a fourth binary system with its eutectic at the intersection with the middle boundary line. In Case 2 the two quintuple points lie on opposite sides of the conjugation line, and therefore both are eutectics and the maximum temperature of the boundary line is located at its intersection with the conjugation line.

Case 3.—The two quintuple points lie on the same side of the conjugation line, but the two quadruple points of the system A-B lie on opposite sides. Since the conjugation line AB-C does not cross the interior boundary line, that line has no maximum point, and the quintuple point which lies outside of its composition triangle C-AB-A is not a eutectic but an alteration point. This is the case where the boundary would form a maximum but the compound AB in contact with certain liquid mixtures ceases to be stable before the maximum is reached, even though this is lower than its stable melting point. Although this quintuple point lies outside the triangle C-AB-A, yet it is an equilibrium point for the three crystalline phases C, AB, and A in contact with a liquid of the composition represented by this point and its vapor. It may be a "hesitation point," however, as the crystalline phase A is disappearing before the composition of the liquid continues on down to the eutectic. The mixtures of C and AB cannot be expressed in a simple binary diagram because of the invasion of the field of A across the conjugation line.

Case 4.—The compound AB is not stable at its melting point (Case 3 of the binary series), and both the quintuple points as well as the quadruple points lie on the same side of

[1] Theorem by Van Rijn van Alkemade (RANKIN and WRIGHT: *loc. cit.*, 17).

the conjugation line. The crystalline phase AB does not appear at all on the liquidus of the binary system C-AB. The quintuple point where the three crystalline phases, C, AB, and A are in equilibrium with liquid and vapor is an alteration point, and the boundary line between the fields of AB and A is called an "alteration curve" in this case.

Case 5.—AB dissociates into crystalline A and crystalline B below the temperature of the binary eutectic and therefore does not appear on the binary liquidus. (See binary case 2.) At lower temperatures in the ternary mixtures, however, a temperature is reached and a field is found where it becomes the primary phase. The ternary system has but one eutectic, which is that quintuple point located at the greater distance from the conjugation line or that quintuple point which lies within its own composition triangle.

Case 6.—Represents a system having a stable ternary compound ABC, as well as a stable binary compound AB. It is simply a combination of four simple ternary systems each having its own ternary eutectic. Very complex ternary systems can be made by combinations of Cases 2, 3, 4, and 5 instead of this simple combination. The ternary compound itself may be stable; may dissociate into two crystalline phases and a liquid, in which case its composition will lie outside its field or may dissociate into three crystalline phases and have no field in which it occurs in equilibrium with the solution.

2. Crystallization

The crystallization curve is a line connecting all points on the temperature-concentration diagram which show the successive composition of the liquid during cooling and crystallization under equilibrium conditions. No phase is removed from the system during the cooling, and the crystallization curve always ends at a quintuple point but may begin at any point on the liquidus. The change in composition of the crystalline portion is entirely different from that of the liquid portion.

Rules of Crystallization.[1]—(1) The initial change in liquid composition of any point in a given field, takes place toward some boundary along the extension of the straight line connecting the composition of the liquid with that of the primary phase of that field.

2. At the boundary line a new crystalline phase appears, and the crystallization curve follows the boundary line to lower temperatures toward a quintuple point.

3. The crystallization curve always ends at that quintuple point which represents the equilibrium between liquid, vapor, and the three solid phases of the three components within whose composition triangle the composition of the original liquid was found.

The Composition of the Crystalline Portion.—(1) The composition of the solid which is crystallizing when the crystallization curve is crossing a field is the primary solid phase of that field. The prolongation of the straight line drawn between any two points on the crystallization curve in the field passes to the primary component of that field.

2. The composition of the solid which is crystallizing at any point on a boundary line is shown by the intersection of the tangent at that point with the line joining the compositions of the two solid phases which are crystallizing at the given point.

3. The mean composition of the solid which has crystallized to any point on the crystallization curve is found by extending the line connecting the given point with the original liquid composition to that line connecting the proper components which will show the average composition.

4. The mean composition of the solid which has crystallized between any two points on the crystallization curve is found by extending the line connecting the two points to intersect the line which will show the average composition of the solid phases.

[1] RANKIN, G. A., and F. E. WRIGHT: "The Ternary System CaO-Al_2O_3-SiO_2," *Am. J. Sci.*, **39**, 51–70 (1915); ANDERSON, OLAF: "The System Anorthite-forsterite-silica," *Am. J. Sci.*, **39**, 426–436 (1915).

5. The mean composition of the final solid is the composition of the original liquid.

Typical Crystallization Curves (Fig. 43).—The crystallization curve of the liquid composition x in the field of B is x-m-f. x lies in the composition triangle C-AB-B. B is the primary solid phase and crystallizes out of the solution

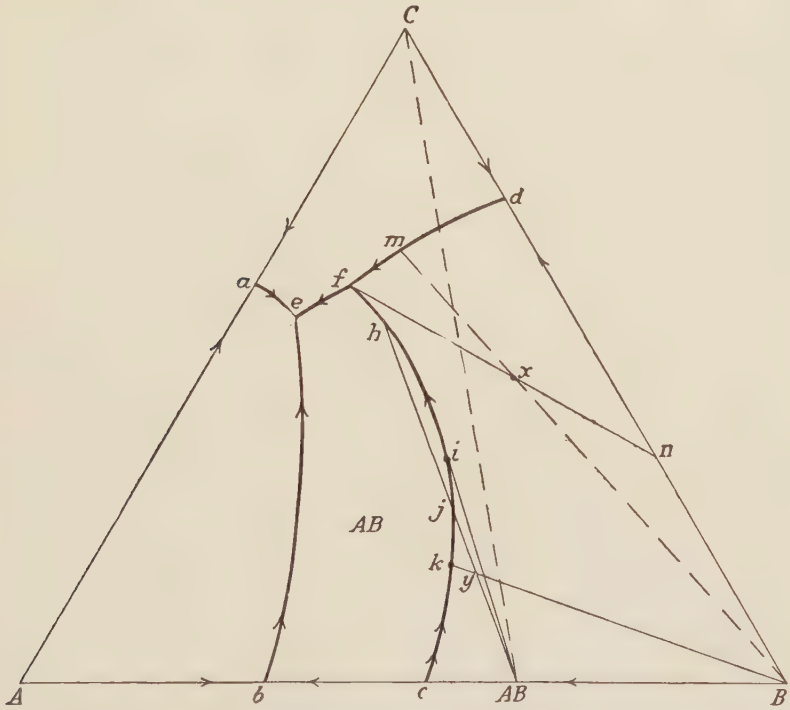


FIG. 43.—Concentration-temperature diagram showing *recurrent crystallization* of a solid phase. (*Anderson, Olaf: Am. J. Sci.*, **39**, 435 (1915).)

as it changes from x to m. m is found by prolonging the line xB to the boundary fd. At m the crystalline phase C appears, and B and C crystallize together from m to f. The ratio of C to B in the solid, which is coming out at any point between m and f, is found by drawing a tangent to the boundary line at that point to intersect the line CB. The crystallization curve stops at f because it is at this quintuple point that crystalline C, AB, and B are in equilib-

rium with liquid and vapor, and the original composition x lies within the triangle C-AB-B. x can be placed in such a position that AB is the second crystalline phase and C does not appear until f.

The mean crystalline composition remains at B from x to m. As the liquid composition changes from m to f and a solid of a composition near that of d is appearing, the mean solid composition changes from B to n, reaching n just as the solution has reached the quintuple point. As the remaining liquid crystallizes, the mean composition of the solid changes from n to x.

All compositions within the triangle C-AB-B will end at f. Compositions represented by points on the line C-AB will crystallize as above except during the crystallization at the point f, where the entire solid B reacts with the remaining liquid to form AB, leaving the two solid phases C and AB. All compositions lying within the triangle C-A-AB will end at the eutectic e.

Recurrent Crystallization of a Solid Phase.—The crystallization curve of the point y is: y-k-j-h-f-e. From y to k, B crystallizes alone; from k to j, B is dissolving and AB is crystallizing, because the tangent at points between j and k intersects only the extension of the line AB-B. The mean composition of the solid starts from B when the liquid composition is at K and reaches AB when the liquid composition has become that represented by j. In other words, the supply of solid B has been exhausted, and AB crystallizes alone as the crystallization curve crosses a portion of the field AB to h. From h to f, AB and B crystallize together. But at the alteration point f all of B again goes into solution. C appears and crystallizes with AB as the composition of the liquid changes from f to e. At the eutectic C, A, and AB crystallize together. During the change in solution composition from f to e the composition of the solid coming out of solution is represented by tangents to ef prolonged to the line C-AB. The mean composition of the solid phase during change from h to f lies between AB and B. During the hesitation

at f it again swings to AB as B dissolves. As the liquid changes from f to e the mean composition travels from AB towards C on the line C-AB and then to y as the phase A crystallizes at the eutectic with C and AB. The crystallization curves of compositions lying in a lower position than y may not meet the boundary line fc but can go directly to ef or eb. The portion of the boundary line fc lying between the tangent point i and c may be called an alteration curve, for it is during the crystallization along these compositions that one solid phase will dissolve while another is crystallizing. Alteration curves are marked with double arrows.

Crystallization in Mixtures Having Solid Solution.[1]— When two compounds form solid solutions they are not only alike in crystalline or optical properties but also have like molecular volumes.[2] The types of temperature-concentration diagrams are different from those described before without solid solution, in that the solidus curve (lower) is not a horizontal line through the eutectic temperature but is a curved line from the melting temperature of one compound to that of the other, or from a possible minimum melting point to both compounds. The isomorphous mixtures of the plagioclase feldspars, albite, $Na_2OAl_2O_36SiO_2$, and anorthite, $CaOAl_2O_32SiO_2$, form one of the most common natural, solid-solution series (Fig. 44). The crystallization of any member of this series may take place in either of two ways:

a. Crystallization with Equilibrium and Free Diffusion.— When the temperature of any composition cools to the liquidus temperature (upper curve), the first crystals formed have the composition represented by the solidus at the same temperature. As the temperature decreases, the crystalline portion not only increases in amount but likewise changes in composition due to reaction with the liquid. The solid composition follows the solidus curve to

[1] Bowen, N. L.: "The Melting Phenomena of the Plagioclase Feldspars," *Am. J. Sci.*, **35**, 597 (1913).

[2] See Chap. VII, p. 208.

the temperature of complete solidification or to that temperature vertically under the starting point on the liquidus curve. The composition of the final solid is therefore that of the original liquid. At the same time, the composition of the liquid has been following the liquidus curve until it reaches a point whose temperature is that of the final solidification point on the solidus curve.

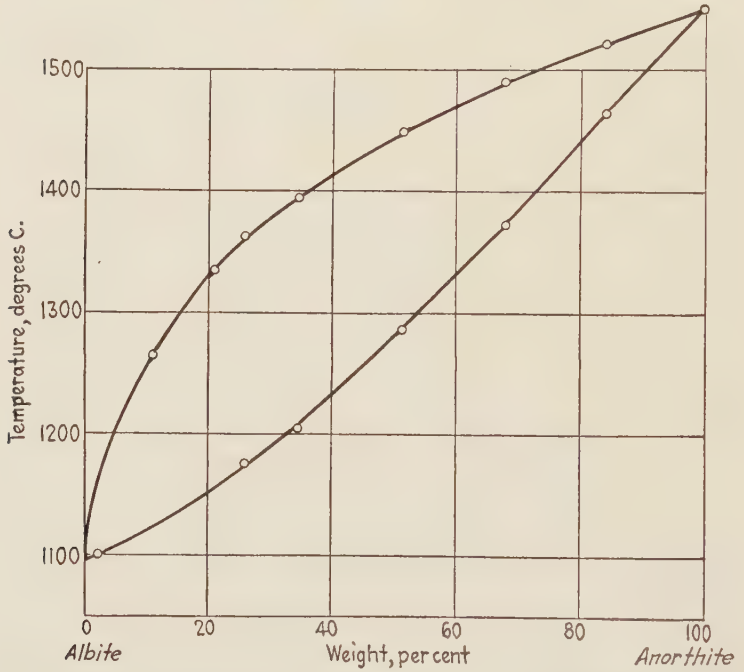


FIG. 44.—Concentration-temperature diagram of the system anorthite-albite (plagioclase series). (*Bowen, N. L.: Am. J. Sci.*, **35**, 583 (1913).)

b. Crystallization with Quick Cooling or in Steps.—If the temperature is suddenly lowered from above that of the liquidus to just below that of the solidus, the whole will solidify as a homogeneous crystalline mass of the final composition. If, however, the cooling takes place in steps or in an irregular fashion without free diffusion or perfect reaction between solid and liquid, separate layers of solid will crystallize out of the field of reaction with the remaining liquid. Consequently, after a series of steps in cooling,

the final liquid may be very rich in the lower melting component and its temperature close to the melting point of that component (albite in the plagioclase series). Such action is found in the cooling of the natural silicates and is one of the reasons for *zoning* of the different minerals. Any mechanical separation of the solid will also prevent further reaction with the remaining liquid.

c. Solid-solution Series with a Minimum Temperature.[1]—Figure 45, showing the temperature-concentration diagram of gehlenite, $2CaOAl_2O_3SiO_2$, and akermanite, $2CaOMgO2$-

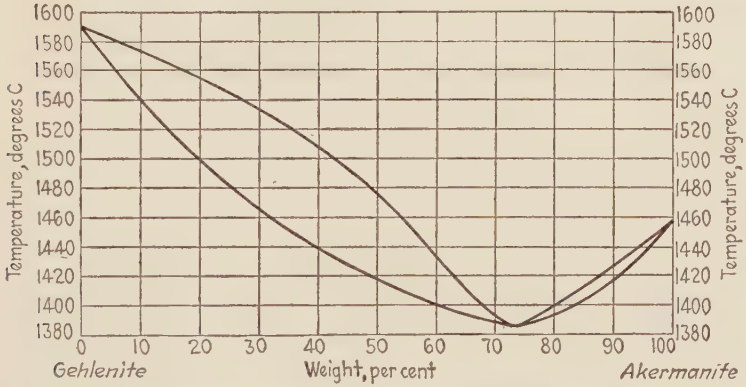


FIG. 45.—Concentration-temperature diagram of the system gehlenite-akermanite. (*Ferguson, J. B., and A. F. Buddington: Am. J. Sci.*, **50**, 133 (1920).)

SiO_2, is an example of a second type of solid-solution diagram. In this case a minimum temperature is found in the series corresponding to the eutectic of the former illustrations.

d. Ternary Systems Having Solid Solutions.[2]—The example shown in Fig. 48 is the system anorthite-albite-diopside, $CaOMgO2SiO_2$. Both the diopside-anorthite and diopside-albite binary systems are simple eutectic systems (Figs. 46, 47), but the anorthite-albite introduces difficulties with its solid solutions. In any system without a ternary eutectic as in Fig. 49, the crystallization curves in the solid-

[1] FERGUSON, J. B., and A. F. BUDDINGTON: "The Binary System Akermanite-gehlenite," *Am. J. Sci.*, **50**, 131 (1920).

[2] BOWEN, N. L.: "The Crystallization of Haplobasaltic, Haplodioritic and Related Magmas," *Am. J. Sci.*, **40**, 161 (1915).

solution field are not straight lines, nor is there any common temperature for the completion of crystallization of all

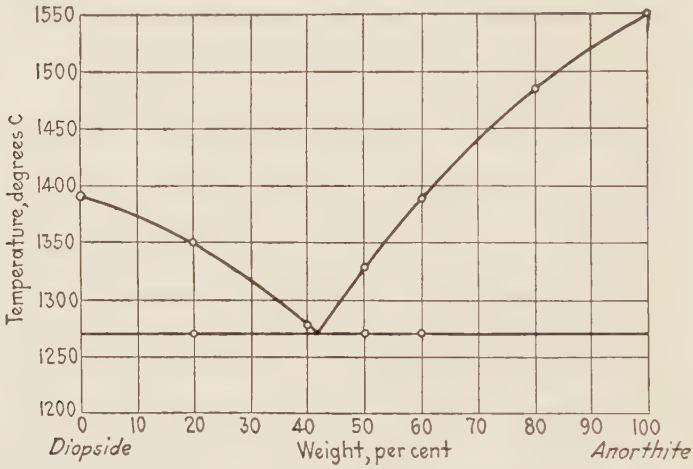


FIG. 46.—Concentration-temperature diagram of the system diopside-anorthite. (*Bowen, N. L.: Am. J. Sci.*, **35**, 577 (1913).)

mixtures of that field. The process of crystallization is followed by a determination of (1) the three-phase bounda-

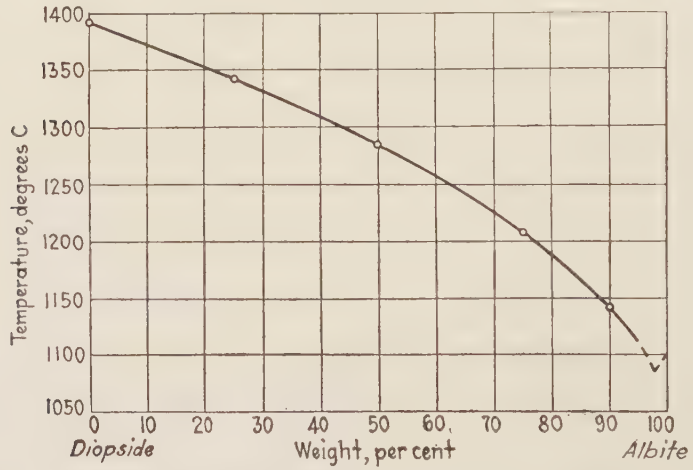


FIG. 47.—Concentration-temperature diagram of the system diopside-albite. (*Bowen, N. L.: Am. J. Sci.*, **35**, 577 (1913).)

ries in the plagioclase field, (2) the refractive indices of the liquids, and (3) the melting points of the different composi-

tions. The three-phase boundaries are the near-parallel lines shown in Fig. 49 angling from the albite-anorthite base to the boundary line between the diopside and plagioclase fields. In Fig. 48 which shows the phase relations at 1230° C. it is found that:

Area *DFEB* is all liquid.

Area *EFG* is liquid *E-F* and plagioclase *K-G*.

Area *ADF* is liquid *D-F* and diopside.

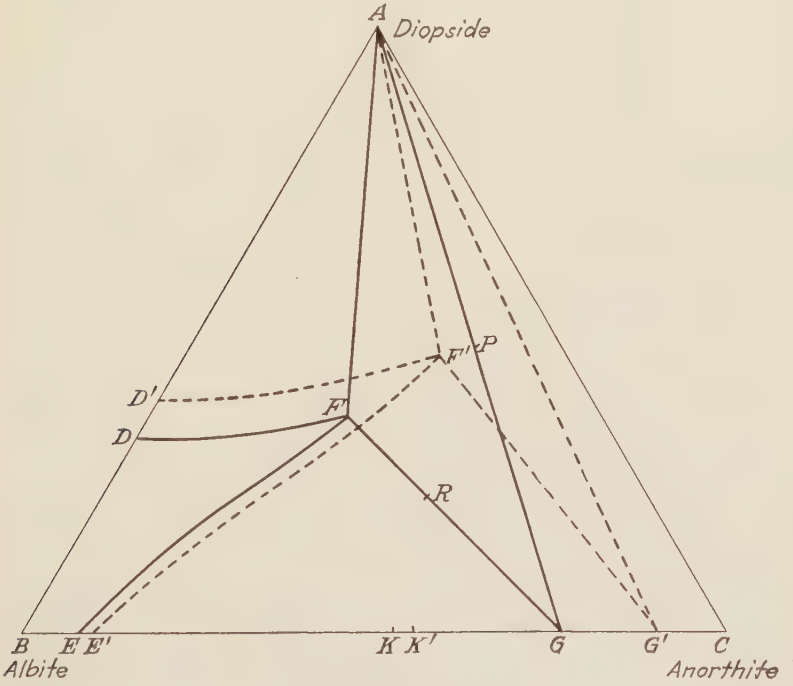


FIG. 48.—Phase relations at 1230° (full lines) and 1250° (broken lines). (*Bowen, N. L.: Am. J. Sci.*, **40**, 171 (1915).)

Area *AFG* is liquid *F*, plagioclase *G* and diopside.

Area *AGC* is plagioclase *G-C* and diopside.

AFG is therefore a *three-phase field.*[1] The boundary line *F-G* is therefore called a *three-phase boundary line*, and can be determined by three methods: (1) determination of the composition of the plagioclase by optical means after hold-

[1] With the gas phase counted, it is a four-phase field in contrast to the three-phase fields (one solid, liquid, and gas) of the former series.

ing at given temperatures to locate the point G; (2) since the line A-G separates a field of solid plagioclase and solid diopside from the three-phase field containing these solids and a liquid, a location of points on this line can be made by noting the temperature at which a given mixture begins to melt; and (3) in a similar manner the boundary of the three-phase field can be located by points on the boundary

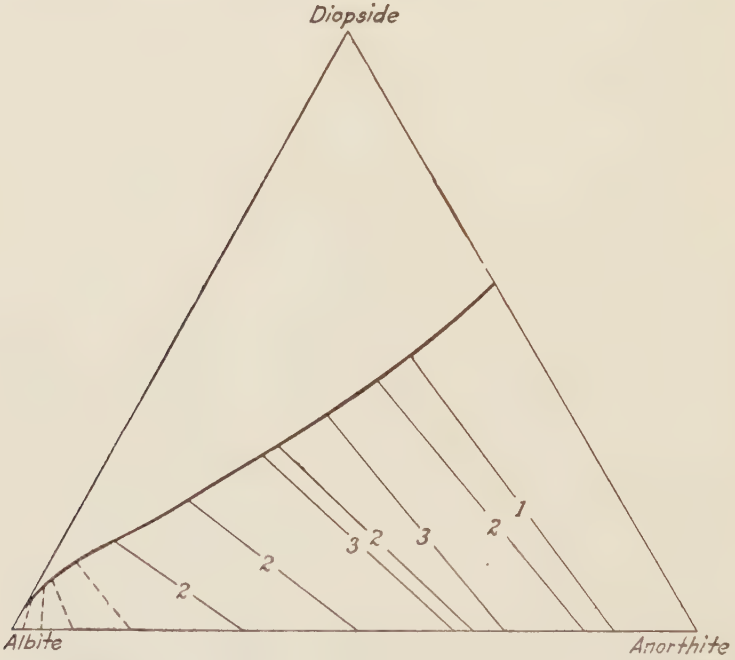


FIG. 49.—Three-phase boundaries. (*Bowen, N. L.: Am. J. Sci.*, **40**, 174 (1915).)

F-G. Field EFG contains no diopside and field AFG does. The determination of the temperature at which diopside appears for a given mixture will therefore locate the boundary line.

Crystallization of Mixtures in the Diopside Field (Fig. 50). The crystallization curve of any liquid composition in the diopside field proceeds to the boundary line between the diopside field and plagioclase field along the extension of the line connecting the given composition with diopside.

It then continues down the boundary line towards the albite corner until the last liquid is exhausted at the point where the plagioclase composition is the same as that of the original; that is, the point of intersection of this boundary curve with the three-phase boundary curve of the original plagioclase composition. The original plagioclase composition is found by extending the line between the original

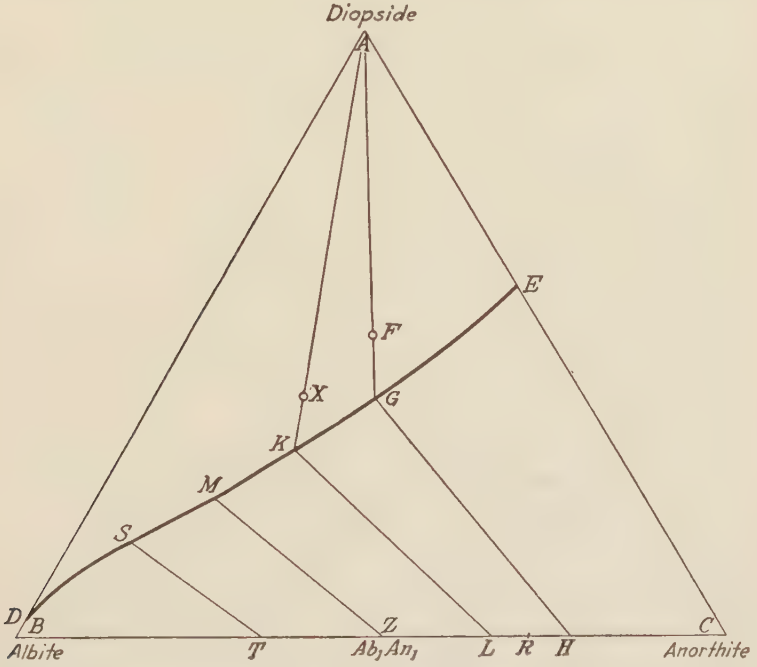


FIG. 50.—Crystallization of mixtures in diopside field. (*Bowen, N. L.: Am. J. Sci.*, **40**, 175 (1915).)

composition and diopside to the plagioclase line at the base of the triangle. Starting with the liquid composition x, diopside will crystallize until k is reached. At this point plagioclase of the compositon l will join the diopside, kl being the three-phase boundary. Continuous reaction with the liquid will change the composition of the plagioclase with lowering temperatures from l so t and the last liquid disappears at s, st being a three-phase boundary

line through t. The amount of solid diopside has also increased during the change from k to s.

Crystallization of Mixtures in the Plagioclase Field. The refractive index of the glass in the binary plagioclase system will give the composition of the liquid in equilibrium with crystals at a given temperature. The *isofracts* (lines of equal refractive index) of Fig. 51 indicate

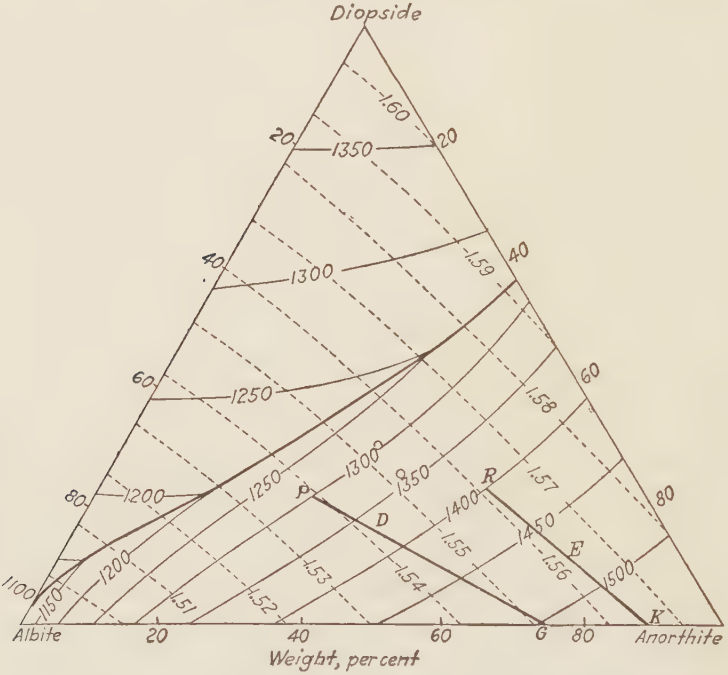


FIG. 51.—Isotherms and isofracts. (*Bowen, N. L.: Am. J. Sci.*, **40**, 178 (1915).)

that in ternary mixtures another factor is needed to fix a given composition. The intersection of the isotherm of the melting temperature with the isofract of the liquid therefore locates the point on the diagram. The crystallization curve of a given point D is given by Bowen[1] as follows: D contains Ab_1An_1 85 per cent, diopside 15 per cent (Fig. 52). This mixture begins to crystallize at 1375° C. with the separation of plagioclase of composition Ab_1An_4

[1] *Loc. cit.*

(see binary diagram 44). The path of crystallization is a curved line passing through P to M for MS is the three-phase boundary line passing through D. Diopside appears at M. The bending of the curve over to P was found by experiment. When the initial liquid D is quenched after holding at 1300° C., the refractive index of the liquid is found to be 1.539, and the point P is the intersection of this

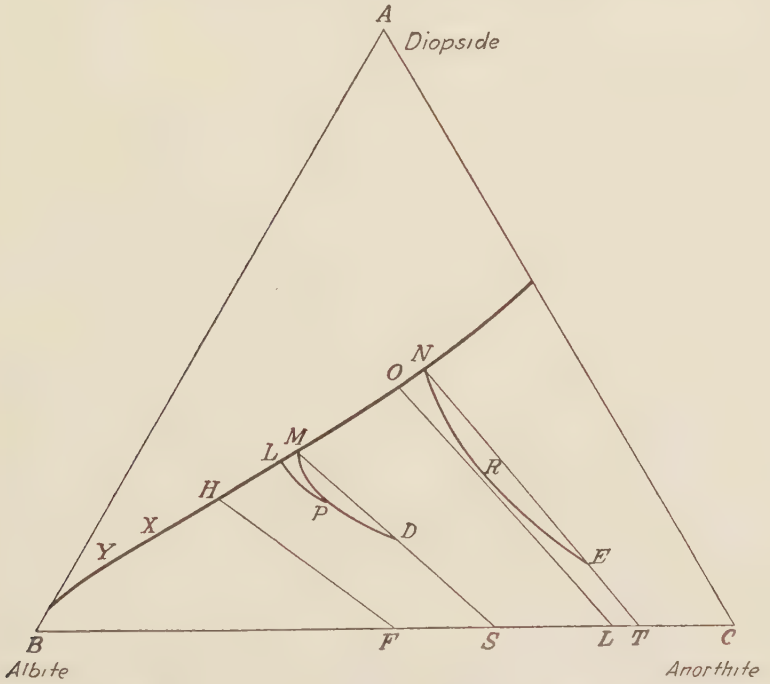


FIG. 52.—Crystallization of mixtures in the plagioclase field. (*Bowen, N. L., Am. J. Sci.*, **40**, 197 (1915).)

insofract with the isotherm 1300°. With further cooling, the crystallization curve follows the boundary line from M to H, with both diopside and plagioclase crystallizing until the composition of the solid plagioclase is again Ab_1An_1, and the last trace of liquid has the composition H, HF being the three-phase boundary line through F. The composition of the plagioclase which has crystallized out in cooling from D to P is found by projecting the line PD to G. If a fresh

study is made by cooling a liquid of the composition P, the crystallization will not follow the crystallization curve of D but will take a curved path of its own to L.

3. Bowen's Reaction Theory[1]

The eutectic system explains the low melting points of mixtures of minerals; it gives an idea of the separation of some minerals from solution, but it does not explain all of the many possible relations between the components in a solution. Solid solutions and incongruent melting change the eutectic relationships, and indeed with the natural silicates such reactions are so common that the simple doctrine of eutexia is of very little use in petrogenesis.

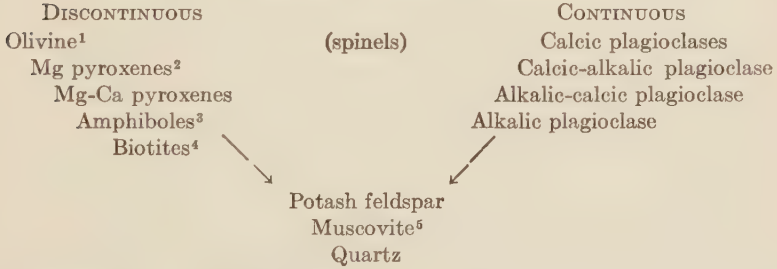
The reaction principle is illustrated by the simple reaction of cooling crystalline plagioclase with the liquid. Such a solid solution-series would be called a *continuous-reaction series*. This same idea is continued with the addition of diopside to the plagioclase. The so-called eutectic boundary curve ED (Fig. 50) is in reality a reaction curve. A true eutectic boundary curve ends in some ternary eutectic point which "represents the composition that all liquids of the system must finally attain and beyond which they never pass."[1] The reaction system is flexible, the final liquid composition depends on the freedom of reaction between crystals and liquid, and zoning, sinking, or other methods of removal of the crystals may change the system and the composition of the final liquid.

A *discontinuous-reaction series* is illustrated by the system MgO-SiO_2 where forsterite reacts with the liquid to form clinoenstatite. If these are not free to react, some liquid will be left over, and varying amounts of silica can be formed when the eutectic crystallizes. Corundum and mullite; leucite and orthoclase constitute other *reaction pairs*. A similar ternary series of discontinuous reactions is found in the series H_2O-K_2SiO_3-SiO_2.

[1] Bowen, N. L.: "The Reaction Principle of Petrogenesis," *J. Geol.* **30**, 177–198 (1922).

The order of separation in the reaction series tends to be fixed or definite while that of the eutectic system varies with the initial composition within the system. For instance, the calcic-rich plagioclase separates before the sodic-rich plagioclase even though the original mixture be high in albite. Likewise, forsterite always separates first although the MgO-SiO_2 solution may be richer in enstatite. In the eutectic series, the component present in the greatest amount above that required for the eutectic separates first. Bowen[1] has therefore expressed the order of separation in natural solutions in the following table which shows the discontinuous series of the left meeting the continuous series on the right at potash feldspar. It means that liquid reacts with olivine to produce pyroxene, with pyroxene to produce amphiboles, and with amphiboles to produce biotites, etc.

TABLE XXV.—REACTION SERIES IN SUBALKALINE ROCKS



[1] Simplest form of olivine is $2MgOSiO_2$.
[2] Simple form of pyroxene is $MgOSiO_2$.
[3] Simple form of amphibole is $CaO3MgO4SiO_2$.
[4] Simple form of biotite is $(H, K)_2O2(Mg, Fe)OAl_2O_33SiO_2$.
[5] Muscovite is $K_2O3Al_2O_36SiO_22H_2O$.

Each mineral has a "reaction relation" to the liquid and tends to change into a later member of the reaction series. The eutectic system is a mere subtraction system. Above potash feldspar the arrangement of the reaction minerals is such that the melting temperatures decrease, but from potash feldspar to quartz the melting temperatures increase.

[1] BOWEN, N. L.: *Loc. cit.*, 190.

4. Typical Concentration-temperature Diagrams of Silicate Mixtures

Silica–Alumina[1] **(Fig. 53).**—The alumina-silica diagram represents a binary system in which the compound mullite, $3Al_2O_32SiO_2$, is unstable above 1810° C. where it melts incongruently, forming corundum and liquid. The final traces of corundum in the mullite composition disappear at 1920°. The eutectic composition of the system is 5.5

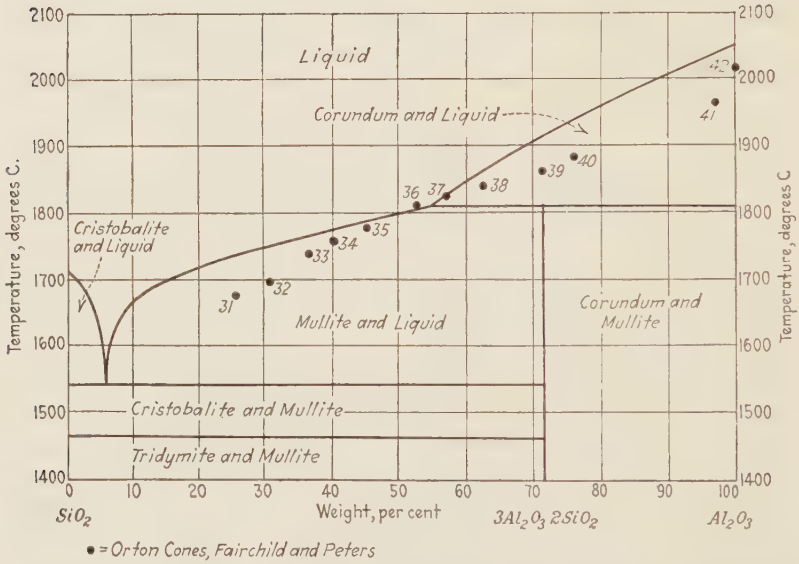


Fig. 53.—Equilibrium diagram of the system alumina-silica. Sillimanite, andalusite, and cyanite, Al_2O_3. SiO_2, dissociate into mullite and cristobalite. (*Bowen, N. L., and J. W. Greig: J. Am. Ceram. Soc.*, **7**, 238–254 (1924).)

per cent alumina and 94.5 per cent silica, and when cooled under equilibrium conditions consists of a mixture of mullite and cristobalite, though with ordinary fast cooling, it is simply glass with traces of mullite crystals. The eutectic temperature, 1545°, is important for all clay and most silicate work, for the silica-alumina ratio of most clays varies from that of the eutectic to that of pure kaolin, $Al_2O_32SiO_2$. It is interesting to compare the eutectic composition

[1] Bowen, N. L., and J. W. Greig: "The System: $Al_2O_3.SiO_2$." *J. Am. Ceram. Soc.*, **7**, 242 (1924).

obtained by Seger[1] in the 1880's by using the cone-fusion method and impure materials with that of the Geophysical Laboratory in 1924, who used the best of furnace, pyrometer equipment, and pure materials in determining the melting point eutectic (Fig. 92*a*). To Fig. 53 has been added the deformation temperatures, recently obtained by the United States Bureau of Standards, for those Orton standard pyrometric cones which consist of mixtures of alumina and silica.

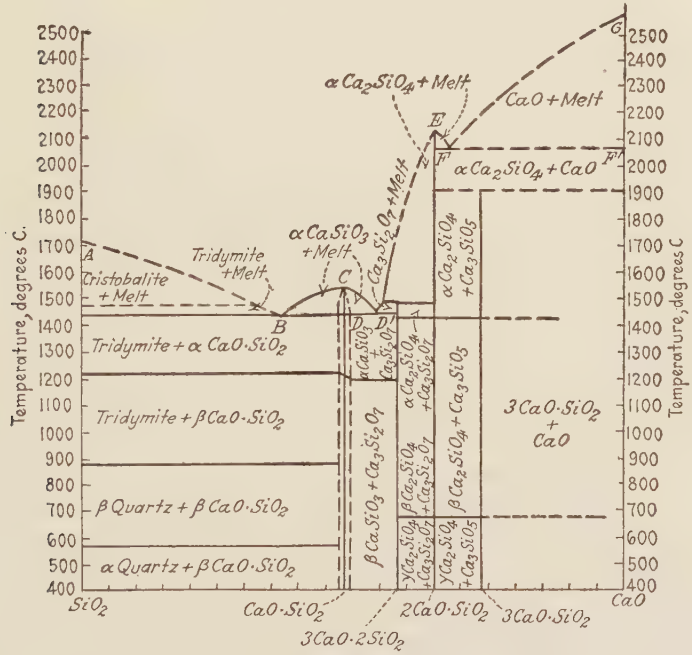


FIG. 54.—Concentration-temperature diagram for the system lime-silica. (*Rankin, G. A., and F. E. Wright: Am. J. Sci.*, **39**, 5 (1915).)

Silica–Lime[2] **(Fig. 54)**.—Four compounds are found in this series: (1) the metasilicate, $CaO.SiO_2$; (2) $3CaO2SiO_2$; (3) the orthosilicate, $2CaO.SiO_2$; and the tricalcium silicate, $3CaO.SiO_2$. Calcium metasilicate occurs in nature as wollastonite, beta $CaO.SiO_2$, and is stable up to 1200° C.

[1] SEGER, H. A.: "Collected Writings." **1**, 545 (1902).

[2] RANKIN, G. A., and F. E. WRIGHT: "The Ternary System CaO-Al_2O_3-SiO_2," *Am. J. Sci.*, **39**, 4–10 (1915).

Pseudo-wollastonite, alpha $CaO.SiO_2$, has been observed only in artificial melts and is stable between 1200° C. and the melting temperature 1540°. The alpha form takes about 2 per cent of either lime or silica into solid solution, and these additions change the inversion temperature as shown on the diagram. The eutectic between pseudo-wollastonite and tridymite has the weight percentage composition of CaO 37, SiO_2 63 with a melting temperature of 1436° C.

The $3CaO2SiO_2$ *compound* forms an eutectic with alpha $CaO.SiO_2$ of the composition: CaO 54.5, SiO_2 45.5, which melts at 1455°. The tricalcium bisilicate melts incongruently at 1475°.

Calcium orthosilicate has a definite melting temperature at 2130°, but occurs in at least three forms, the alpha, beta, and gamma. Alpha changes to beta at 1420° and beta to gamma at 675° C. The latter change is accompanied by an increase of about 10 per cent in volume, which accounts for the *dusting* often found in cooling portland cement mixtures.[1]

Tricalcium silicate does not appear on the liquidus curve but dissociates at 1900° into CaO and $2CaO.SiO_2$. This is below the eutectic temperature, 2065°, between lime and the orthosilicate. The eutectic composition is CaO 67.5 and SiO_2 32.5.

Lime–Alumina[2] (**Fig. 55**).—Four compounds occur: (1) tricalcium aluminate, $3CaO.Al_2O_3$, which dissociates into CaO and liquid at 1535° C.; (2) $5CaO3Al_2O_3$, congruent melting temperature of 1455° C.; (3) calcium aluminate, congruent melting temperature 1600°; and (4) $3CaO5Al_2O_3$ with a congruent melting temperature of 1720° C. The 5:3 and the 3:5 compounds have both stable and unstable forms.

[1] Klein, A. A., and A. J. Philips: "Hydration of Portland Cement," *U. S. Bur. Standards, Tech. Paper*, **43** (1914).

Bates, P. H., and A. A. Klein: "Calcium Silicates and Calcium Aluminates in Normal Portland Cement," *U. S. Bur. Standards, Tech. Paper*, **78** (1917).

[2] Rankin and Wright: *loc. cit.*, 10–13.

The eutectic between the 3:1 and 5:3 compounds has the composition of CaO 50, Al_2O_3 50 and a melting temperature of 1395°. That between 5:3 and 1:1 is composed of CaO 47, Al_2O_3 53, and melts at 1400° C. That between 1:1 and 3:5 is composed of CaO 33.5, Al_2O_3 66.5, and melts at 1590°. The eutectic between 3:5 and alumina has a composition of CaO 24, Al_2O_3 76, and melts at 1700°.[1]

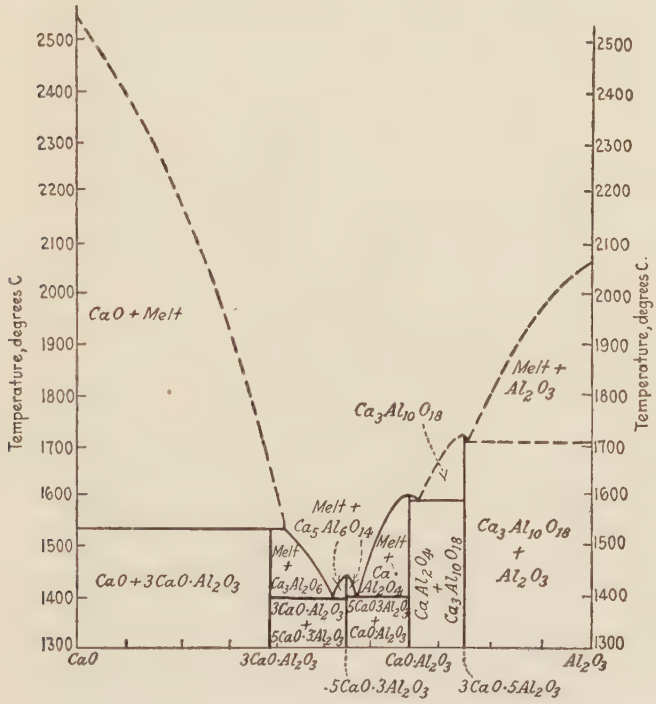


Fig. 55.—Concentration-temperature diagram for the system lime-alumina. (*Rankin, G. A., and F. E. Wright: Am. J. Sci.*, **39**, 11 (1915).)

Magnesia–Silica[2] **(Fig. 56)**.—Compounds: the orthosilicate forsterite, $2MgO.SiO_2$ (1890° C.) and clinoenstatite, $MgO.SiO_2$ which melts incongruently at 1557° C.

Eutectics: cristobalite-clinoenstatite, SiO_2 12.5, $MgO.SiO_2$ 87.5, 1554°. Periclase-forsterite, MgO 14, forsterite 86, 1850°.

[1] Rankin and Wright: *loc. cit.*, 10–13.

[2] Bowen, N. L., and Olaf Anderson: *Am. J. Sci.*, **37**, 488 (1914).

Magnesia–Alumina[1] (**Fig. 57**).—Compounds: spinel, $MgO.Al_2O_3$, 2135° C. Eutectics: spinel-magnesia MgO,

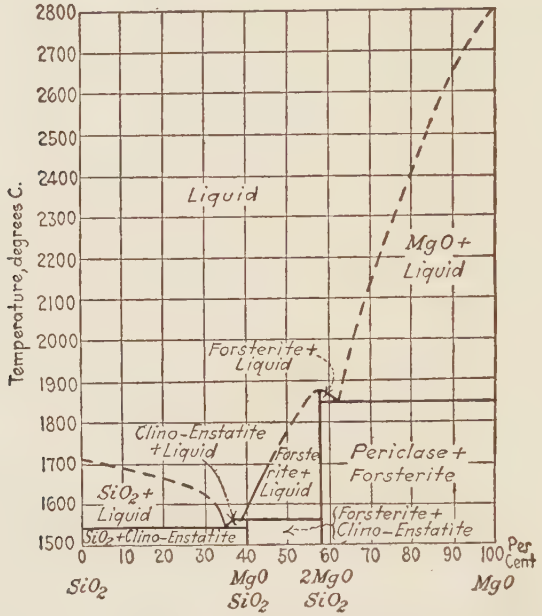


Fig. 56.—Concentration-temperature diagram of the system SiO_2-MgO. (*Bowen, N. L., and Olaf Anderson: Am. J. Sci.*, **37**, 488 (1914).)

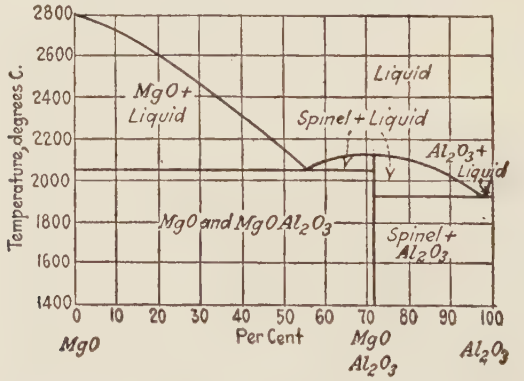


Fig. 57.—Temperature-concentration diagram of the system MgO-Al_2O_3. (*Rankin and Merwin: Am. J. Sci.*, **45**, 304 (1918).)

45, Al_2O_3 55, 2030° C.; spinel-alumina, alpha alumina 98, magnesia 2, 1925° plus or minus 40°, and beta alumina 92,

[1] Rankin and Merwin: *Am. J. Sci.*, **45**, 304 (1918).

magnesia 8, 1925° plus or minus 40° C. Spinel forms a nearly complete series of solid solutions with alpha alumina. Beta alumina seems to take a small amount of spinel into solid solution. The series has not been definitely developed.

Lime–Alumina–Silica[1] (**Fig. 58**).—Ternary compounds: anorthite, $CaO.Al_2O_32SiO_2$, 1550°; gehlenite, $2CaO.Al_2O_3.SiO_2$, 1590° C. Eutectics: No. 2, CaO 23.25, Al_2O_3 14.75,

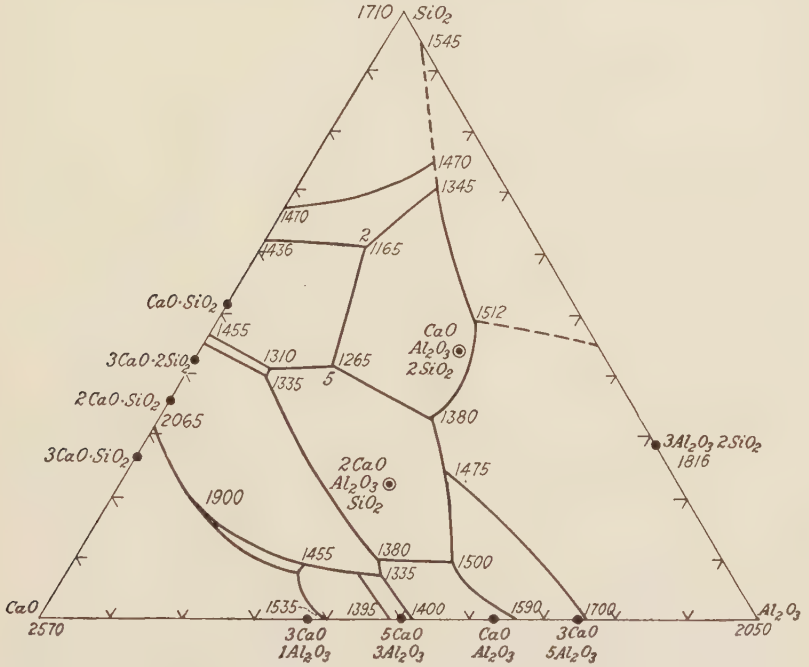


FIG. 58.—Temperature-concentration diagram of the system $CO\text{-}AL_2O_3\text{-}SiO_2$. (*Rankin and Wright: Am. J. Sci.*, **39**, 40 (1915).)

SiO_2 62.00, 1165° C.; No. 5, CaO 38, Al_2O_3 20, SiO_2 42, 1265° C. Numerous other eutectics, quadruple and quintuple points.

Magnesia–Alumina–Silica[2] (**Fig. 59**).—Ternary compounds: cordierite, $2MgO2Al_2O_35SiO_2$, unstable. Ternary eutectic: MgO 20.3, Al_2O_3 18.3, SiO_2 61.4, 1345° C.

[1] RANKIN and WRIGHT: *Am. J. Sci.*, **39**, 40 (1915).
[2] RANKIN, G. A., and H. E. MERWIN: *Am. J. Sci.*, **45**, 301 (1918).

Lime–Magnesia[1] **(Fig. 60).**—Binary eutectic: CaO 67, MgO 33, 2300° C.

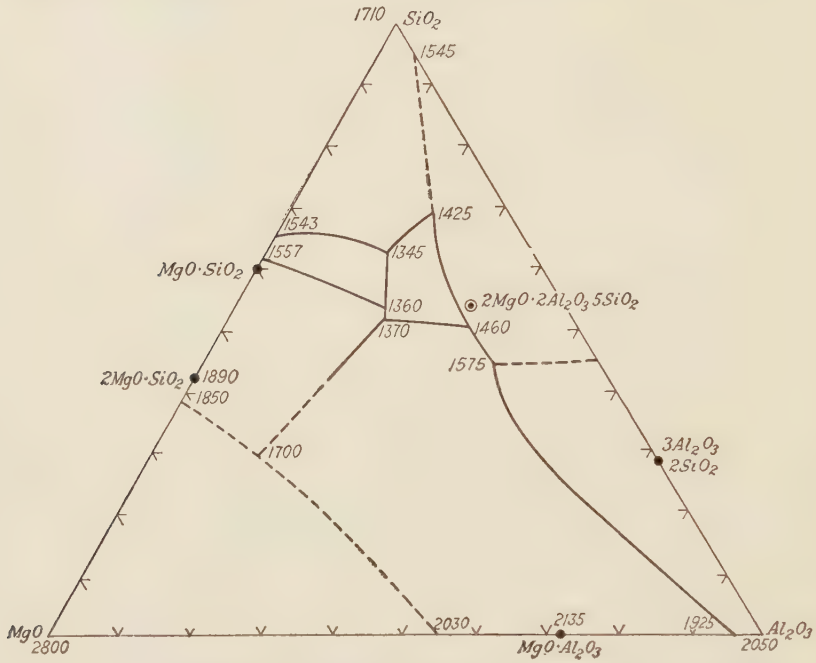


FIG. 59.—Temperature-concentration diagram of the system MgO-Al_2O_3-SiO_2. (*Rankin and Mervin: Am. J. Sci.*, **45**, 301 (1918).)

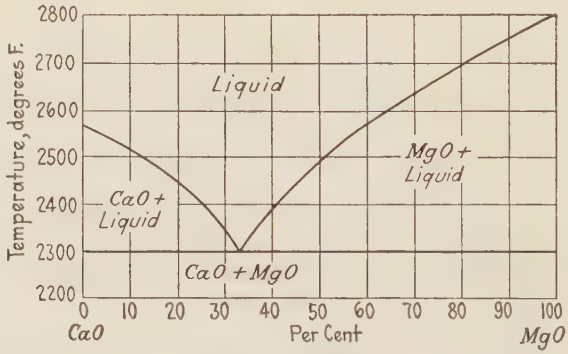


FIG. 60.—Temperature-concentration diagram for the system CaO-MgO. (*Rankin and Merwin: J. Am. Chem. Soc.*, **38**, 571 (1916).)

Silica–Lime–Magnesia[2] **(Fig. 61).**—Ternary eutectic: CaO 30.6, MgO 8.0, SiO_2 61.4, 1320° C.

[1] RANKIN and MERWIN: *J. Am. Chem. Soc.*, **38**, 571 (1916).

[2] FERGUSON, J. B., and H. E. MERWIN: *Am. J. Sci.* (4), **48**, 81 (1919).

Magnesia–Lime–Alumina[1] (**Fig. 62**).—Ternary eutectics: point (2) CaO 51.0, Al_2O_3 42.7, MgO 6.3, 1345°; point (3) CaO 41.5, Al_2O_3 51.8, MgO 6.7, 1345° C.

Silica–Anorthite[2] (**Fig. 64**).—Binary eutectic: SiO_2 48, anorthite 52, 1353° C.

Fosterite–Anorthite[3] (**Fig. 65**).—The *A-B* and *C-D* portions of the curve represent the binary series while



FIG. 61.—Temperature-concentration diagram of the system SiO_2-CaO-MgO. (*Ferguson and Merwin: Am. J. Sci.* (4), **48,** 81 (1919).)

B-C is a portion of the quaternary system MgO-CaO-Al_2O_3-SiO_2 where spinel is the primary phase. Consequently the mixtures *B-C* cannot be expressed in terms of the binary system. Point *B* contains forsterite 14, anorthite 86, and melts at 1444° C. Point *C* contains forsterite 46, anorthite, 54, and melts at 1466° C.

[1] RANKIN, G. A., and H. E. MERWIN: *J. Am. Chem. Soc.*, **38,** 568 (1916).
[2] ANDERSON, OLAF: *Am. J. Sci.*, **39,** 421 (1915).
[3] ANDERSON, OLAF: *Am. J. Sci.*, **39,** 424 (1915).

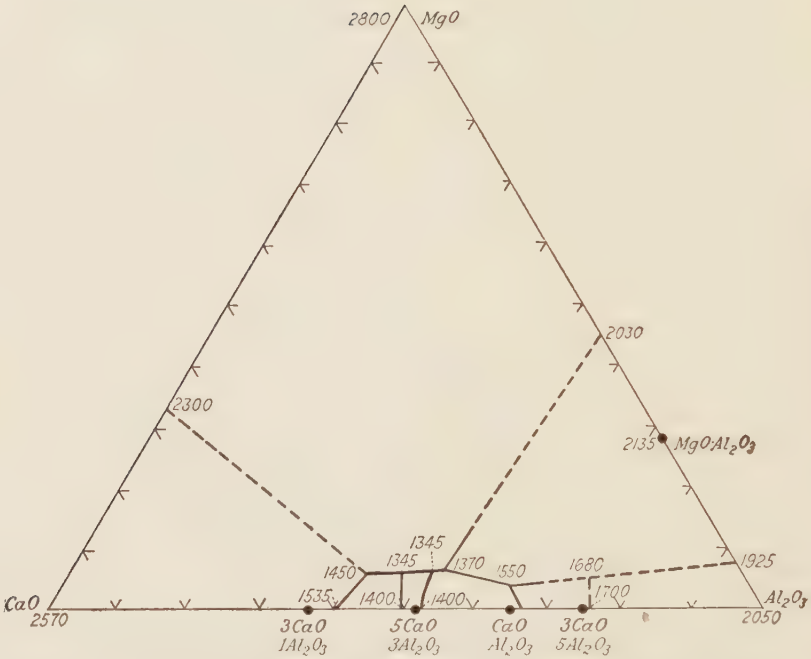


FIG. 62.—Temperature-concentration diagram of the system Mgo-CaO-Al_2O_3. (*Rankin and Merwin: J. Am. Chem. Soc.*, **38**, 568 (1916).)

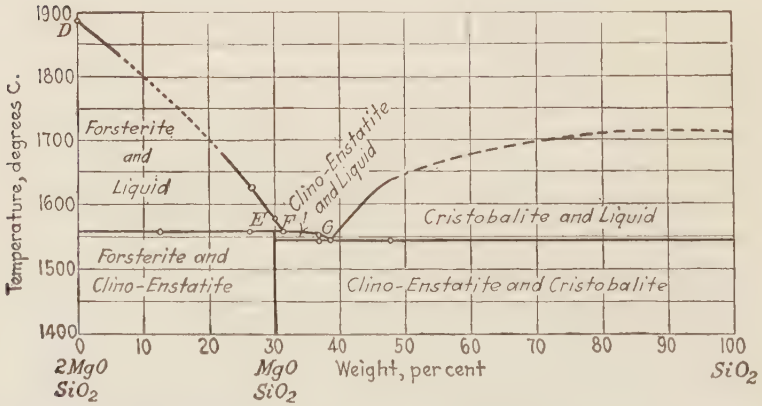


FIG. 63.—Concentration-temperature diagram of the system forsterite-silica. (*Bowen, N. L., and Olaf Anderson: Am. J. Sci.*, **487**, 495 (1914).)

Anorthite–Forsterite–Silica[1] **(Fig. 66).**—Ternary eutectic: silica 33, forsterite 16.5, anorthite 50.5, or SiO_2 61.9, Al_2O_3 18.51, CaO 10.15, and MgO 9.44, 1222° C.

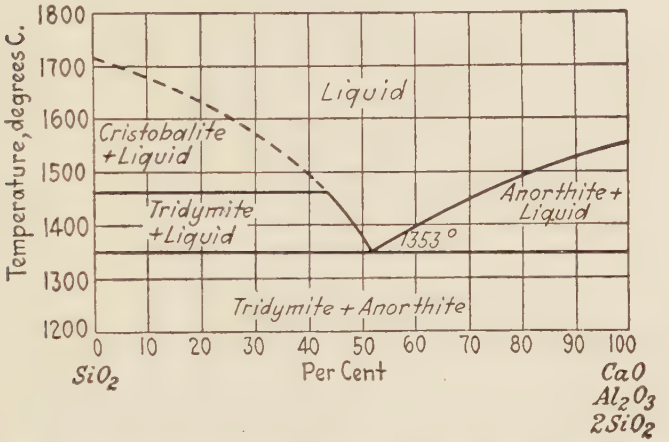


Fig. 64.—Concentration-temperature diagram of the system silica-anorthite. (*Anderson, Olaf: Am. J. Sci.*, **39**, 421 (1915).)

Spinel invades the ternary diagram by crystallizing as the primary phase near the forsterite-anorthite boundary

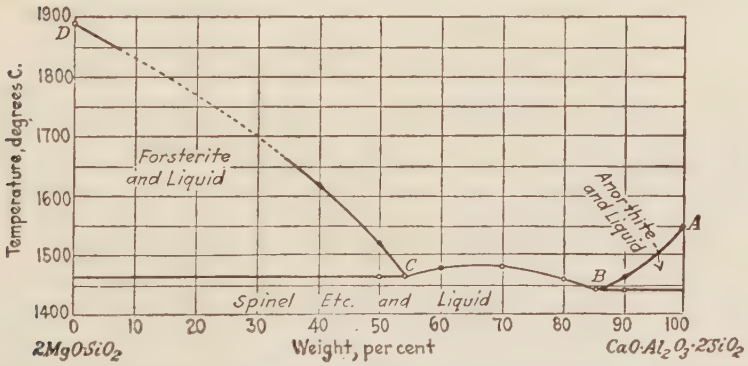


Fig. 65.—Concentration-temperature diagram of the system forsterite-anorthite. (*Anderson, Olaf: Am. J. Sci.*, **39**, 424 (1915).)

line, but it cannot be properly considered in terms of the ternary system. The alteration point (1260° C.) between

[1] Anderson, Olaf: *loc. cit.*

clino-enstatite-anorthite and forsterite has the composition An 55, Fo 25.5 SiO_2 19.5

Diopside–Forsterite–Silica[1] **(Fig. 67).**—Clino-enstatite and diopside form a complete series of solid solutions and therefore have a common field. No ternary eutectic exists and the binary eutectic between diopside and silica is the lowest point of formation of liquid.

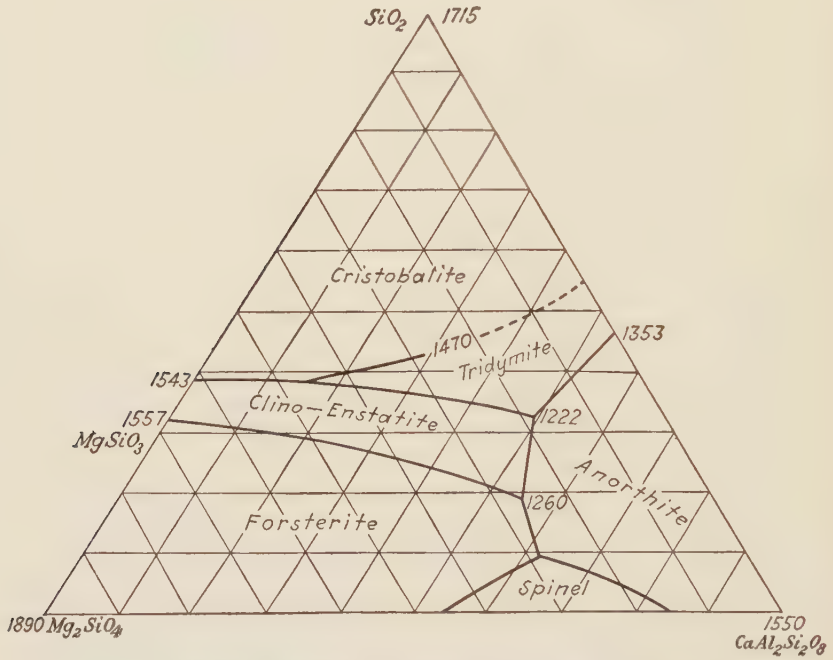


Fig. 66.—Concentration-temperature diagram of the system anorthite-forsterite-silica. (*Anderson, Olaf: Am. J. Sci.*, **39**, 440 (1915).)

Silica–Sodium Metasilicate[2] **(Fig. 68).**—The binary compound Na_2O2SiO_2, 874° C., forms the eutectic $Na_2O.SiO_2$ 77, SiO_2 23, 840° C. with $Na_2O.SiO_2$ and the eutectic, $Na_2O.SiO_2$ 53, SiO_2 47, 793° C. with silica. The melting temperature of $Na_2O.SiO_2$ is 1088° C.

[1] Bowen, N. L.: *Am. J. Sci.*, (4), **38**, 207 (1914).

[2] Morey, G. W., and N. L. Bowen: *Trans. Soc. Glass Tech.*, **9**, 240 (1925).

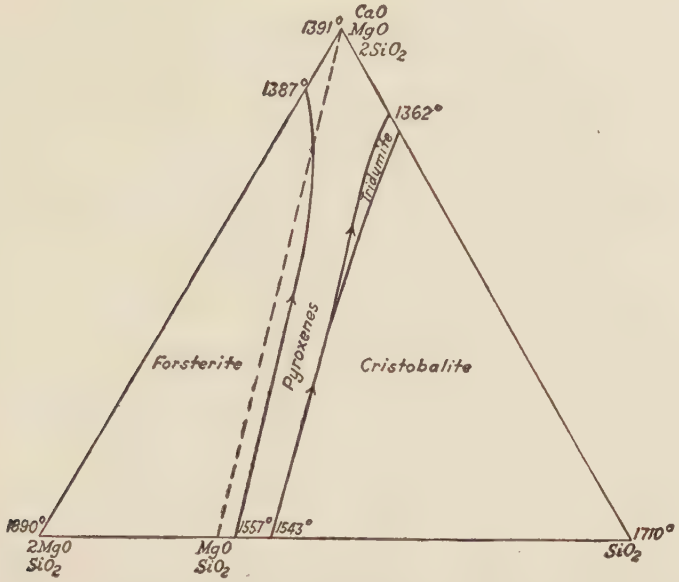


FIG. 67.—Concentration-temperature diagram of the system diopside-forsterite-silica. (*Am. J. Sci.* (4) **38**, 207 (1914).)

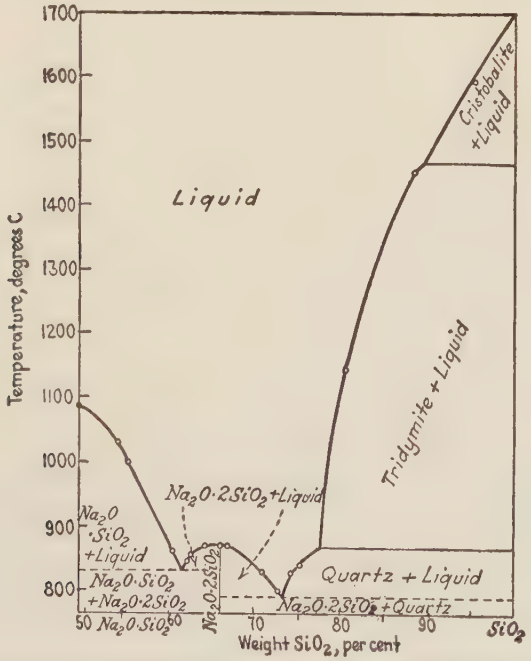


FIG. 68.—Temperature-concentration diagram of the system Na_2O, SiO_2-SiO_2. (*Morey, G. W., and N. L. Bowen: Trans. Soc. Glass Tech.*, **9**, 240 (1925).)

Sodium Metasilicate–Calcium Metasilicate[1] **(Fig. 69).**—Compound $Na_2O2CaO3SiO_2$ has a congruent melting temperature at 1284° C. It forms the eutectic containing about 33.5 per cent CaO, 1282° C. with $CaO.SiO_2$. The compound $2Na_2OCaO3SiO_2$ is unstable above 1141° C., but forms the eutectic containing 3 per cent CaO, 1060° C. with $Na_2O.SiO_2$.

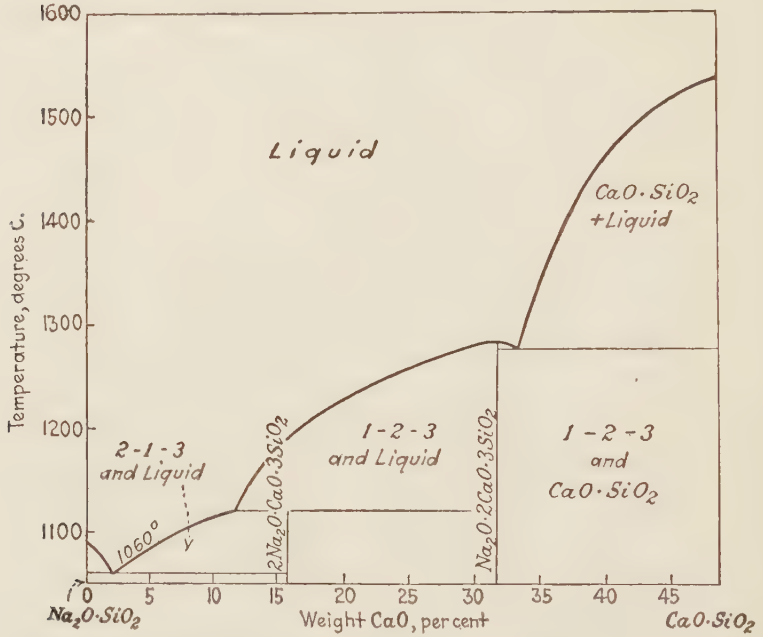


FIG. 69.—Concentration-temperature diagram of the system Na_2O, SiO_2–CaO, SiO_2. (*Morey, G. W., and N. L. Bowen: Trans. Soc. Glass Tech.*, **9**, 248 (1925).)

Silica–Calcium Metasilicate–Sodium Metasilicate[1] **(Fig. 70).**—Besides the ternary eutectics mentioned above, the compound $Na_2O3CaO6SiO_2$, found in the field of calcium metasilicate, is unstable above 1045°. The ternary eutectic CaO 5.2, SiO_2 73.5, Na_2O 21.3, 725° has the lowest melting temperature of the series although another eutectic (*k*) is found between $Na_2O.SiO_2$, Na_2O2SiO_2, and the (2, 1, 3) compound.

[1] Same as 2, p. 242.

Water–Potassium Metasilicate–Silica[1] **(Fig. 71).**—Compounds: potassium hydrogen disilicate $K_2O.H_2O4SiO_2$ (515° C.); potassium disilicate, K_2O2SiO_2 (1041° C.); potassium disilicate monohydrate, $K_2O.H_2O2SiO_2$ (melts incongruently at 405° C.); potassium metasilicate, $K_2O.SiO_2$, 966° C.; potassium metasilicate hemihydrate, $K_2O.0.5H_2O.SiO_2$, stable between 370 and 610° C.; potassium metasilicate monohydrate, $K_2O.H_2O.SiO_2$, stable between

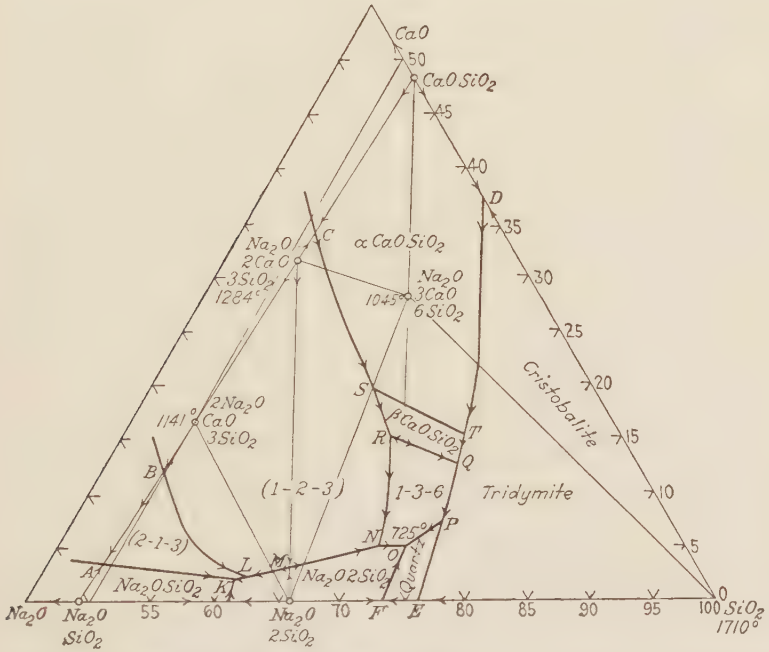


Fig. 70.—Concentration-temperature diagram of the system SiO_2-$CaOSiO_2$-Na_2OSiO_2. (*Morey, G. W., and N. L. Bowen: Trans. Soc. Glass Tech.*, **9**, 233 (1925).)

200 and 370° C. Eutectics: K_2O 55, SiO_2 45, 775° C., between $K_2O.SiO_2$ and K_2O2SiO_2; and K_2O 28, SiO_2 72, 525° C. between K_2O2SiO_2 and SiO_2.

Leucite–Silica[2] **(Fig. 72).**—Orthoclase becomes unstable at 1170°, changing into leucite and liquid. The last of

[1] Morey, G. W., and C. N. Fenner: *J. Am. Chem. Soc.*, **38**, 1180 (1917).
[2] Morey, G. W., and N. L. Bowen: *Am. J. Sci.*, **4**, 10 (1922).

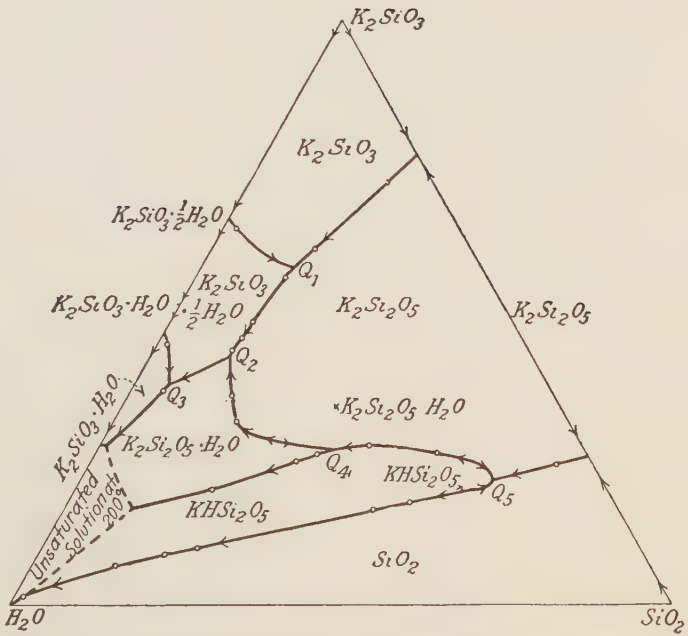


FIG. 71.—Concentration-temperature diagram of the system, H_2O-K_2SiO_3-SiO_2. (*Morey, G. W., and C. N. Fenner: J. Am. Chem. Soc.*, **39**, 1180 (1917).)

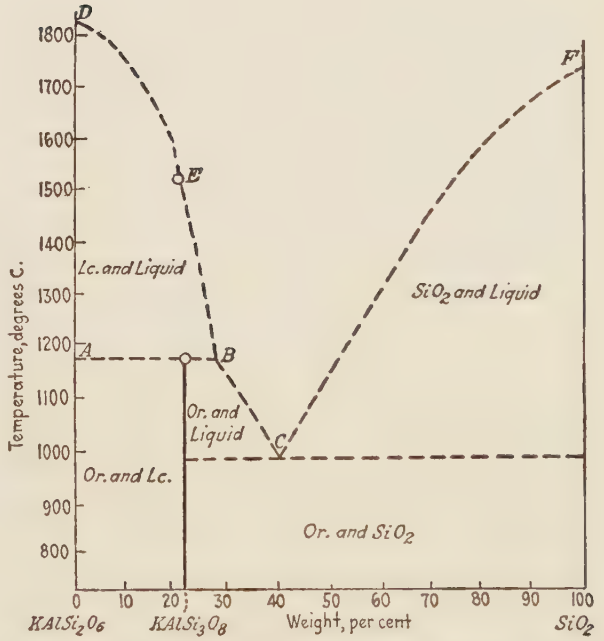


FIG. 72.—Concentration-temperature diagram of the system leucite-silica including orthoclase. (*Morey, G. W., and N. L. Bowen: Am. J. Sci.*, **4**, 10 (1922).)

the leucite dissolves at 1530° C. Orthoclase forms the eutectic, approximately 40 per cent SiO_2 and 60 per cent leucite, 990° C. with silica.

Barium Oxide–Silica[1] **(Fig. 73)**.—Compounds: barium disilicate, $BaO2SiO_2$, 1426° C.; dibarium trisilicate, $2BaO\text{-}3SiO_2$, 1450°; barium metasilicate, $BaOSiO_2$, 1604° C.; barium orthosilicate, $2BaO.SiO_2$. Eutectics: BaO 47.0

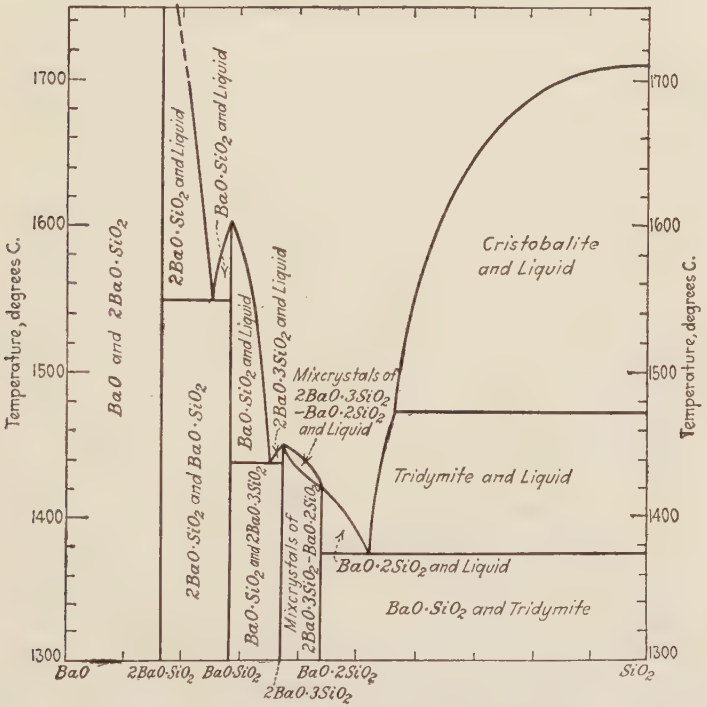


Fig. 73.—Concentration-temperature diagram of the system barium oxide-silica. (*Eskola, P.: Am. J. Sci.* (5) **4**, 345 (1922).)

SiO_2 53.0, 1374° C., between tridymite and $BaO2SiO_2$; BaO 60, SiO_2 40, 1435°; BaO 74.5, SiO_2 25.5, 1551°.

Solid solutions are formed between dibarium trisilicate and barium disilicate.

Strontium Oxide–Silica[2] **(Fig. 74)**.—Compounds: strontium metasilicate, $SrO.SiO_2$, 1580° C., and strontium

[1] Eskola, P.: *Am. J. Sci.*, **4**, 345 (1922).

[2] Eskola, P.: *Am. J. Sci.* (5), **4**, 336 (1922).

orthosilicate, $2SrO.SiO_2$. Eutectics: SrO 46.5, SiO_2 53.5, 1358° C., between tridymite and strontium metasilicate; SrO 65.5, SiO_2 34.5, 1545° C.

Lime–Ferric Oxide[1] **(Fig. 75).**—Compounds: dicalcic ferrite, $2CaO.Fe_2O_3$ melts incongruently at 1436° C.; monocalcic ferrite, $CaO.Fe_2O_3$ dissociates at 1216° C. The eutectic between $CaO.Fe_2O_3$ and Fe_2O_3 has the composition of 8 per cent CaO, 92 per cent Fe_2O_3, and a melting temperature of 1203° C.

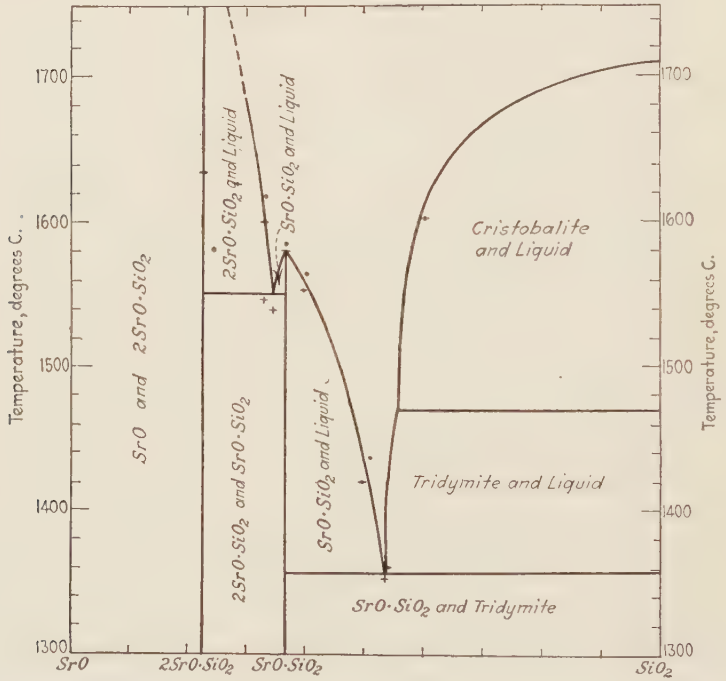


FIG. 74.—Concentration-temperature diagram of the system strontium oxide-silica. (*Eskola, P.: Am. J. Sci.* (5) **4**, 336 (1922).)

Zirconia–Silica[2] **(Fig. 76).**—Compounds: zircon, $ZrO_2.SiO_2$, 2550° C. An eutectic probably occurs between zircon and zirconia with a melting temperature of about

[1] SOSMAN, R. B., and H. E. MERWIN: *J. Wash. Acad. Sci.*, **6**, 532–537 (1916).

[2] WASHBURN, E. W., and E. E. LIBMAN: *J. Am. Ceram. Soc.*, **3**, 638 (1920).

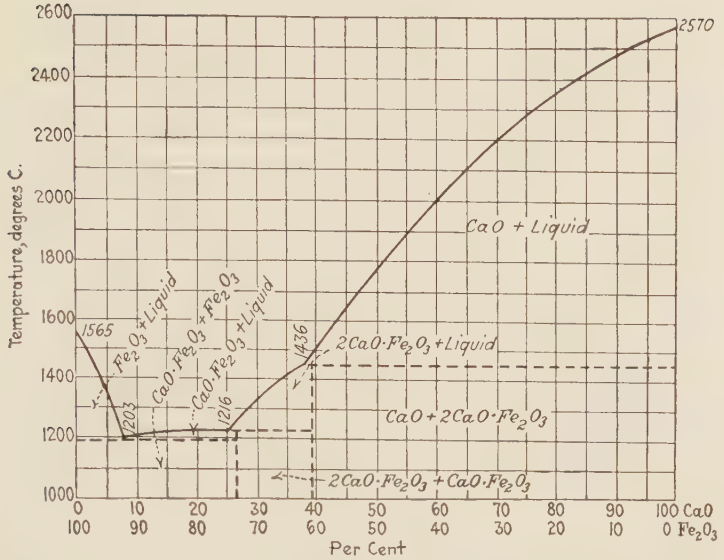


FIG. 75.—Concentration-temperature diagram of the system CaO-Fe_2O_3. There are two calcium ferrites, dicalcic ferrite, $2CaOFe_2O_3$, and the monocalcic ferrite, $CaOFe_2O_3$, with dissociation temperatures at 1436° and 1216° C., respectively. (*Sosman and Merwin: J. Wash. Acad. Sci.*, **6**, 532–537 (1916).)

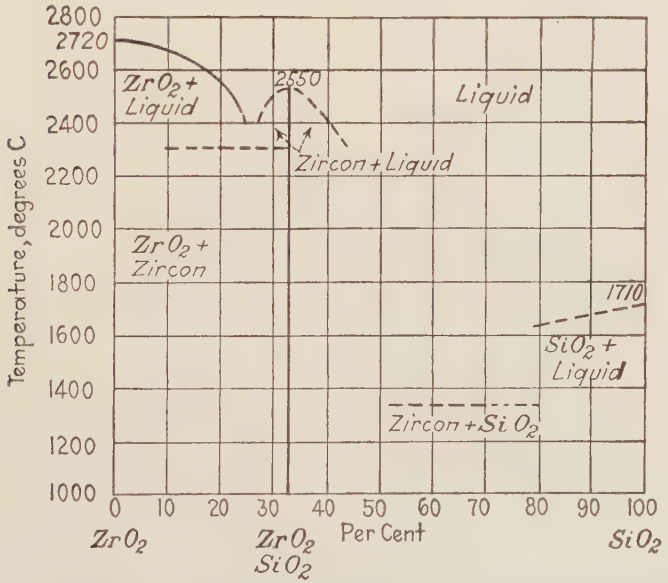


FIG. 76.—Concentration-temperature diagram of the system zirconia-silica. (*Washburn, E. W., and E. E. Libman: J. Am. Ceram. Soc.*, **3**, 638 (1920).)

2300° C. An eutectic likewise probably exists between zircon and cristobalite at an unknown temperature.

5. Some Minerals Encountered in Silicate Fusions

Table XXVI.—Probable Artificial Glasses (Rapid Cooling)

SiO_2	SiO_2, quartz, tridymite, and cristobalite
K_2O	$K_2O.SiO_2$, potassium metasilicate
	$K_2O.SiO_2½H_2O$
	$K_2O.SiO_21H_2O$
	$K_2O2SiO_21H_2O$
	K_2O2SiO_2
	$K_2O4SiO_2H_2O$
	$K_2O.Al_2O_32SiO_2$, kaliophilite
	$K_2O.Al_2O_34SiO_2$, leucite
	$K_2O.Al_2O_36SiO_2$, orthoclase and microcline
	Possible potassium-lime silicates
Na_2O	$Na_2O.SiO_2$, sodium metasilicate
	Na_2O2SiO_2
	$Na_2O.Al_2O_32SiO_2$, nephelite,[1] carnegieite[2]
	$Na_2O.Al_2O_36SiO_2$, albite
	$Na_2O3CaO6SiO_2$
	$Na_2O2CaO3SiO_2$
	$2Na_2O.CaO3SiO_2$
PbO	$PbO.SiO_2$, lead metasilicate
	$2PbO.SiO_2$, lead orthosilicate

Probable Artificial Crystals (Rapid Cooling)

Al_2O_3	Al_2O_3, corundum
	$3Al_2O_32SiO_2$, mullite
CaO	$CaO.SiO_2$, wollastonite
	$3CaO2SiO_2$, tricalcium disilicate
	$2CaO.SiO_2$, calcium orthosilicate
	$3CaO.SiO_2$, tricalcium silicate
	$3CaO.Al_2O_3$, tricalcium aluminate
	$5CaO3Al_2O_3$
	$CaO.Al_2O_3$, calcium aluminate
	$3CaO5Al_2O_3$
	$CaO.Al_2O_32SiO_2$, anorthite
	$2CaO.Al_2O_3SiO_2$, gehlenite
MgO	MgO, periclase
	$MgO.SiO_2$, clino-enstatite
	$2MgO.SiO_2$, forsterite
	$MgO.Al_2O_3$, spinel
	$2MgO2Al_2O_35SiO_2$, cordierite
CaO-MgO	$CaO.MgO.2SiO_2$, diopside
	$2CaO.MgO.2SiO_2$, akermanite
	$5CaO2MgO6SiO_2$
	$CaO.MgO.SiO_2$, monticellite

TABLE XXVI.—PROBABLE ARTIFICIAL CRYSTALS (RAPID COOLING).—(*Continued*)

ZnO	$ZnO.SiO_2$, zinc metasilicate
	$2ZnO.SiO_2$, willemite
CaO-PbO	$PbO2CaO3SiO_2$, margarosanite
BaO	$BaO.SiO_2$, barium metasilicate
	$2BaO.SiO_2$, barium orthosilicate
	$BaO2SiO_2$, barium disilicate
	$2BaO3SiO_2$, dibarium trisilicate
	$BaO.Al_2O_32SiO_2$, celsian
CaO-BaO	$2CaO.BaO3SiO_2$, dicalcium barium silicate
SrO	$SrO.SiO_2$, strontium metasilicate
	$2SrO.SiO_2$, strontium orthosilicate

[1] Stable below 1248° C.
[2] Stable above 1248° C.

6. MELTING OR SOFTENING TEMPERATURES OF REFRACTORY MATERIALS

TABLE XXVII

Name	Formula	Melting or fusion temperature, degrees Centigrade	Authority
Carbon	C	3700	
Magnesia	MgO	2800	Kanolt
Thoria	ThO_2	2790	Ruff
Zirconia	ZrO_2	2700	Washburn
Lime	CaO	2572	Kanolt
Zircon	$ZrO_2.SiO_2$	2550	Washburn
Beryllium oxide	BeO	2410	Ruff
Yttria	YtO	2410	Ruff
Chromite	$FeOCr_2O_3$	2180	Kanolt
Spinel	$MgOAl_2O_3$	2135	Rankin and Merwin
Alumina	Al_2O_3	2050	Kanolt
Silicon carbide	SiC	Forms 1840 Dissociates 2240	Tucker and Lampen
Chromium oxide	Cr_2O_3	1990	Kanolt
Mullite	$3Al_2O_32SiO_2$	1816 (incongruent)	Bowen
Kaolin	$Al_2O_32SiO_2$	1755	Kanolt[1]
Platinum	Pt	1755	Kanolt
3:5 calcium aluminate	$3CaO5Al_2O_3$	1725	Rankin and Merwin
Silica	SiO_2	1710	Merwin and Ferguson
Rutile	TiO_2	1700	Kanolt
Calcium aluminate	$CaO.Al_2O_3$	1587	Rankin and Merwin

[5] Other temperatures for kaolin vary from 1745 to 1790° C.

G. DEFORMATION, SOFTENING, AND FUSION OF SILICATES AND CLAYS

Deformation or softening, in this case, is the change from a rigid to a fluid condition by the application of heat. Fusion likewise means the production of a fluid, but the term conveys the idea of interaction between two or more substances, that is, a fluxing action. Deformation may

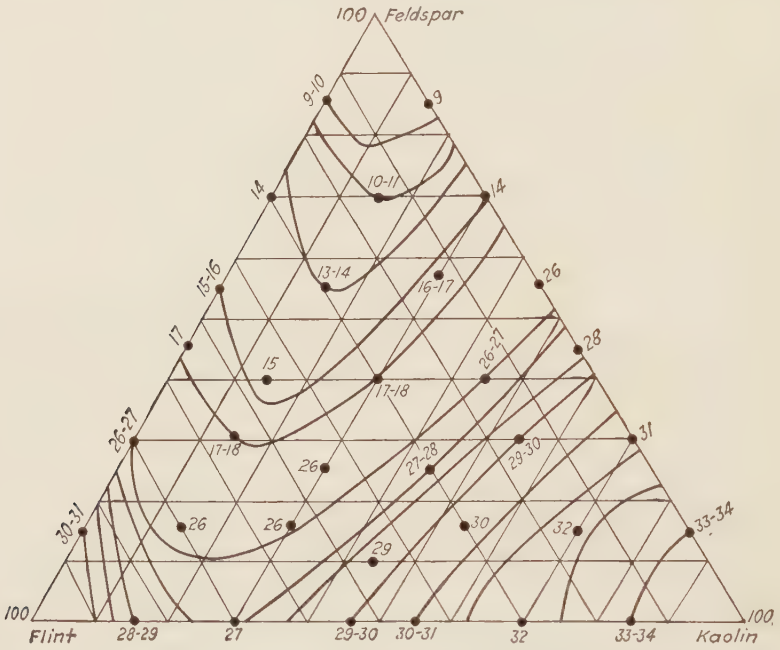


FIG. 77.—Cone deformation point diagram of the system feldspar-silica-kaolin expressed in terms of the old German pyrometric cones. (*Simonis, M.: Sprechsaal*, No. 40 (1907).)

also include the change of shape or form of the pyroplastic silicate due to the application of an exterior pressure. A large number of silicate minerals and their mixtures have slow melting or softening intervals. This retarded action may be due to several causes:

1. A chemical compound such as quartz or albite has a definite or congruent melting temperature, but the liquid produced is so viscous that a distinct time interval is necessary to produce the complete change from the crystalline to

the amorphous fluid condition. Eutectics fall in this same class of no-temperature range. With some materials it may be necessary to raise the temperature that the viscosity of the resulting amorphous body may be low enough to cause noticeable signs of flow or softening. In most cases the time interval alone is sufficient to cause deformation. If the mass is appreciable, the heat of melting may retard the softening.

2. A definite chemical compound melts incongruently, changing into another solid with liquid. Orthoclase and mullite are in this class. At the incongruent melting temperature a certain amount of liquid is produced, which may be sufficient in amount and low enough in viscosity to produce deformation. In order to completely eliminate all of the new or second solid phase, however, it is necessary to raise the temperature; thus, deformation may proceed without the change of all crystalline to amorphous material. The first case is similar to a block of ice on a hot sidewalk. The liquid forms on the surface and fluid runs down the sides, leaving fresh crystalline surfaces exposed. In the second case the liquid may form throughout the mass and cause internal deformation. A splinter of microcline feldspar will bend like a cone of amorphous material when heated; but a splinter of mullite will melt like a splinter of ice, no doubt because the liquid formed at the incongruent melting temperature has low viscosity. The liquid formed must be very fluid, since mullite crystallizes with great rapidity and small crystals or mat surfaces can be produced even when the melts are quenched in air or water.

3. A mixture of two or more solid compounds when heated to the eutectic temperature produces a certain amount of liquid by interaction or fusion. The mass will deform when, with the increase of temperature above that of the eutectic, the amount of this liquid and its fluidity are sufficient to cause internal lubrication. This case is similar to (2) except that the mixtures may be very complex. The softening of silicate mixtures is therefore a function of time and temperature. A lower temperature

interval will be required as the composition of the mixture approaches that of the eutectic. Loss of shape undoubtedly takes place with most mixtures before the liquidus tem-

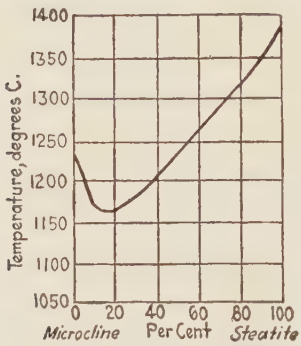


FIG. 78.

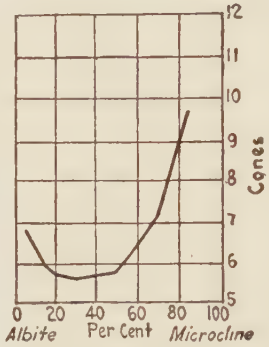


FIG. 79.

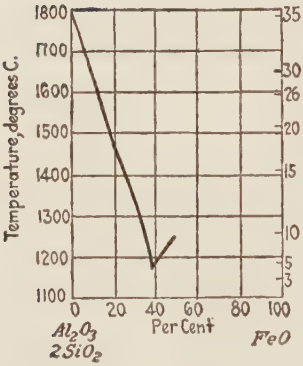


FIG. 80.

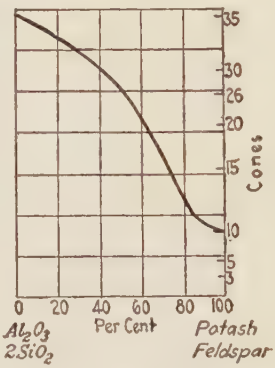


FIG. 81.

FIG. 78.—Deformation-concentration diagram of the system microcline feldspar-steatite, $3MgO4SiO_2H_2O$. The temperature of cone deformation was noted with a pyrometer. (*Howat, W. S.: Trans. Am. Ceram. Soc.*, **18,** 489 (1916).)

FIG. 79.—Deformation-concentration diagram of the system microcline-albite. The cone deformation was noted by standard cones. (*Watts, A. S.: Trans. Am. Ceram. Soc.*, **15,** 153 (1913).)

FIG. 80.—Deformation-concentration diagram of the system $Al_2O_32SiO_2$-FeO. The cone deformation was noted by the older German standard cones. (*Rieke: Sprechsaal*, No. 16 (1910).)

FIG. 81.—Deformation-concentration diagram of the system $Al_2O_32SiO_2$-potash feldspar. The cone deformation was noted by standard cones. (*Simonis, M.: Sprechsaal*, No. 40 (1907); *Wilson, Hewitt: Trans. Am. Ceram. Soc.*, **15,** 229 (1913).)

perature is attained. The isomorphous system, anorthite-albite has a similar fusion range even though there is no

eutectic and in this case reaction causes a continual change in composition of both liquid and solid.

In the commercial heating of ceramic bodies the temperature is usually raised continuously to a maximum. It is common practice, however, in the development of the final degree of vitrification to hold the temperature constant for

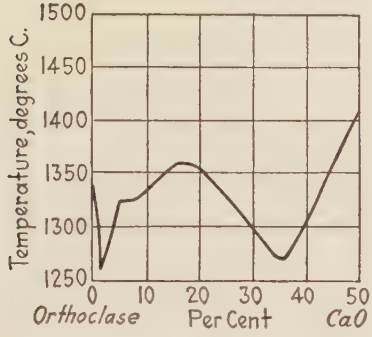


FIG. 82.

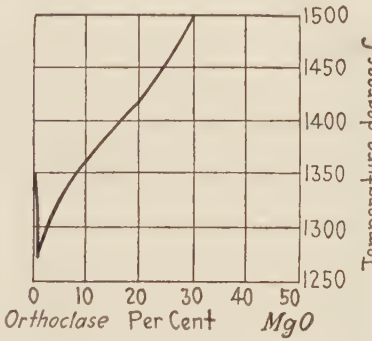


FIG. 83.

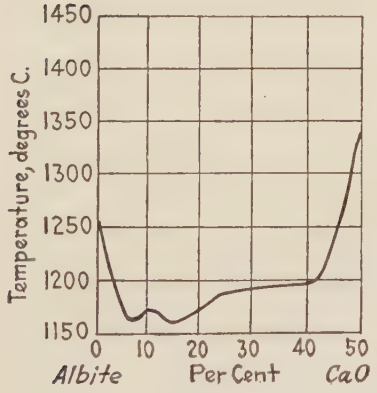


FIG. 84.

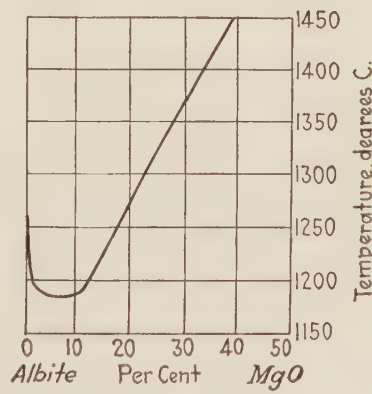


FIG. 85.

FIGS. 82, 83, 84, and 85.—Deformation-concentration systems orthoclase-CaO, orthoclase-MgO; albite-CaO and albite-MgO. Cone deformations were measured by a pyrometer. (*Kirkpatrick, F. A.: Trans. Am. Ceram. Soc.*, **18**, 575–618 (1916).)

a given interval or to "soak the heat" to that portion of the kiln with the lowest temperature. This is the best method for the production of uniform conditions in all parts of the common type of periodic kilns, and at the same time it pro-

vides the time element necessary for the completion of vitrification or partial fusion.

Ceramic practice is not interested in the theoretical "melting" of the minerals accompanying clays unless the melting is accompanied by a change in rigidity which may effect a change in the structure of the clay mass. Deformation is sharply defined for only a few silicates, and, in the case of the heterogeneous mixtures of amorphous and crystalline material called "clay," it usually covers a considerable temperature interval. Clay products are heated to a condition of only partial fusion. A reduction of volume is needed to produce a dense, vitrified structure in clay wares, but a change of shape is not wanted and cannot be controlled. A still more desirable body would be that which has the requisite shape, size, and density in the dry condition and merely requires the action of heat to develop strength and hardness. Some of the talc and similar magnesium silicate mixtures molded under very high pressures are reported to be of this nature.

Glass, glazes, and enamels are ceramic mixtures which are carried beyond the vitrified and into the fluid condition. It is with these products that the data on melting and fusion of silicates is most applicable at the present time. Cone fusion tests merely give data on the beginnings of fusion or flow, however, and most glasses and glazes are carried to a far more fluid condition where the viscosity must be measured by other means. Fusion data are likewise necessary in the development of electric-furnace melting and crystallization of the new superrefractory compounds.

1. Factors Affecting the Fusion of Silicates

The temperature at which clays or silicate mixtures will soften or fuse, together with the progress of fusion depends on their chemical and mineralogical composition; their molecular arrangement; the size and state of aggregation of the particles and grains; the intimacy of mixing and uniformity of composition; the density and porosity of the structure to be heated; the rate of heating; the expulsion of

vapor and internal gases; the absorption and retention of furnace gases; the composition of the furnace gases; the pressure applied while heating; and the rate of increase in fluidity near the softening temperature.

Common clays are mixtures of many compounds—some are stable at high temperatures, others, like kaolin and feldspar, break down with the application of heat, and still others, like quartz, invert to other crystalline forms of the same chemical composition. The fusion of common clay is a combination of both congruent and incongruent melting together with eutectic and other reactions, all of which may proceed at the same time because of the usual lack of uniformity, homogeneity, and intimate contact of the units in the mass.

For many years, able investigators disagreed in the determination of the melting point of pure silica, the most common oxide on the earth's surface (neglecting hydrogen oxide) and obtained results varying from 1625 to 1825° C. Siliceous materials are very viscous at temperatures near their melting and softening temperatures. Clays high in silica and low in fluxes give good service in many branches of the refractory industry. Such clays resist deformation under load better than many aluminous materials which have higher softening temperatures.[1] When compared with other fluxes, potash feldspar, $K_2O Al_2O_3 6SiO_2$, which is likewise high in silica, is a slow and safe fluxing medium because of its high viscosity during fusion. $K_2O SiO_2$ is more viscous than $Na_2O\ SiO_2$. FeO produces more fluidity than MgO, and CaO will lower the viscosity of most clay mixtures at temperatures close to their fusion points. In other words, the ability of the common oxides to impart characteristic viscosity effects in different compositions at fusion

[1] Silica brick made from quartzite and containing 95 per cent silica withstand pressure at high temperatures better than kaolin, magnesia, chrome, bauxite, and diaspor brick, although the softening point of the silica brick is much lower than the others. For this reason, silica brick alone can be used in the roofs of open-hearth steel furnaces. This property, however, is due to the well-developed structure of interlocking crystals of cristobalite and tridymite.

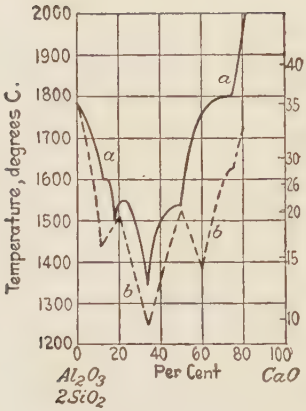


FIG. 86.

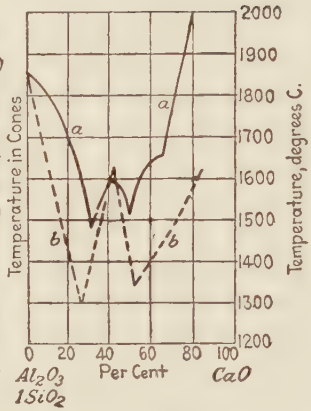


FIG. 87.

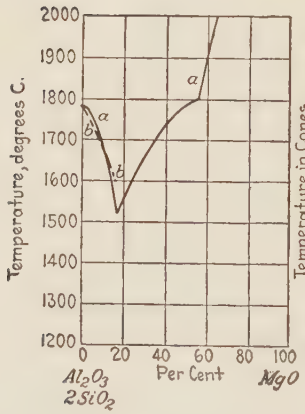


FIG. 88.

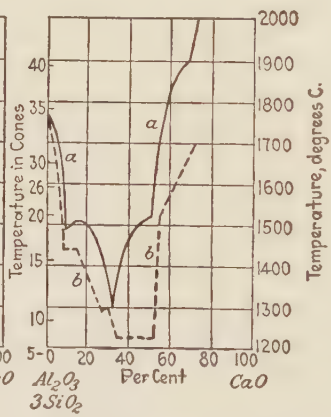


FIG. 89.

FIG. 86.—*a*, temperature-concentration diagram of the system $Al_2O_3 2SiO_2$-CaO. (*Rankin and Wright: Am. J. Sci.*, **39**, 40 (1915).) Curve *b* is the deformation-concentration diagram. Deformation of cones was determined by the use of the older German cones. (*Rieke: Sprechsaal*, Nos. 37, 38, 1906; 45, 46, 1907; *also see Bleininger, A. V.: U. S. Bur. Stand., Tech. Paper* 7, 31 (1912) *and Beecher, M. F.: Iowa State College, Eng. Exp. Sta., Bull.* 40, 39, 40 (1915).)

FIG. 87.—*a*, temperature-concentration diagram of the system $Al_2O_3SiO_2$-CaO. (*Rankin and Wright: loc. cit.*) *b*, deformation-concentration curve. (*Rieke: loc. cit.*)

FIG. 88.—*a*, temperature-concentration diagram of the system $Al_2O_3 2SiO_2$-MgO. (*Rankin, G. A. and H. E. Merwin: Amer. J. Sci.*, **45**, 322 (1918).) *b*, deformation-temperature diagram. (*Rieke: loc. cit.*)

FIG. 89.—*a*, temperature-concentration diagram of the system $Al_2O_3 3SiO_2$-CaO. (*Rankin and Wright: loc. cit.*) *b*, temperature-deformation diagram. (*Rieke: loc. cit.*)

temperatures is an individual property as peculiar to the individual as other physical properties.

The determination of the deformation point of a silicate is then but the determination of some arbitrarily fixed viscosity value. That value which has been universally adopted by ceramists to mean "complete deformation" is represented by a cone of the substance so softened that the top has bent over level with the base. This is a condition far beyond the best vitrification or useful period for most clay products and estimations regarding the service or action of the clay at lower temperatures can be made only by comparison.

2. Pyrometric Cones

The cone system consists of a series of 57 small tetrahedrons made of varying silicate compositions which are placed in the kiln with clay products to indicate the temperatures and progressive heat effect on clay wares. They are numbered from 022 to 01 and from 1 to 42, similar to the time system of B.C. and A.D. The high-temperature series are also used to indicate the degree of refractoriness of fire clays.

Lauth and Vogt of Sèvres, France, are credited[1] with the invention made in 1882. The system was not used for general work, however, until Herman A. Seger, director of the research laboratory of the Royal Porcelain Factory at Berlin, Germany, devised in 1886 a series of mixtures which were the original Seger cone series and form the basis of the present system. Cone manufacture was started in the United States in 1896 by Edward Orton, Jr., then Professor of Ceramic Engineering at the Ohio State University. The manufacture has been continued to the present time at a private laboratory and factory in Columbus, Ohio.

Cones 022 to 20 are $2\frac{3}{4}$ inches high. Each face is $\frac{9}{16}$ inch at the bottom and $\frac{3}{32}$ inch at the top. Cones 23 to 42 are only 1 inch high, with faces $\frac{5}{16}$ inch at the bottom and

[1] Orton, Jr., Edward: *Standard Pyrometric Cone Catalogue* (1917).

1/16 inch at the top. The temperatures of deformation range in fairly regular intervals from 585 to 2015° C.

The Deformation of a Cone.—The bending of a cone may be divided into three stages as follows: the first may be called the "vitrification stage" in which an open, porous body is changed to a vitreous or glass-like structure. The cone loses its organic bond, moisture, chemically combined water, carbon dioxide and other gases, and decreases in

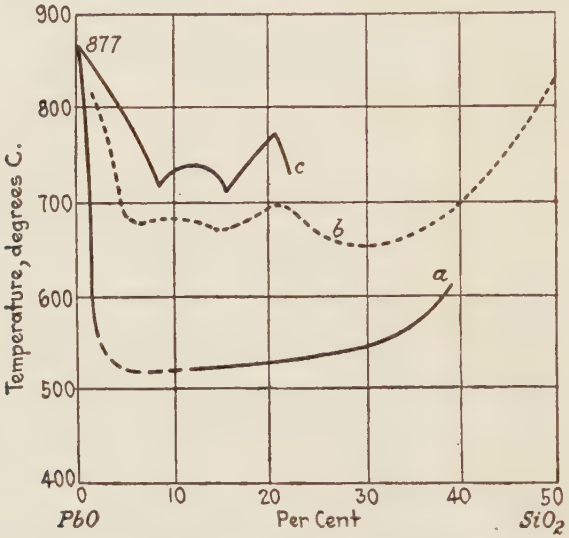


FIG. 90.—Deformation-concentration diagram of the system PbO-SiO_2. *a*, deformation temperatures were noted with a pyrometer. (*Mellor, J. W., A., Latimer, and A. D. Holdcroft: Trans. Eng. Ceram. Soc.*, **9**, 126 (1909).) *b*, cone deformation curve. (*Lu, K. C.: J. Am. Ceram. Soc.*, **9**, 40 (1926).) *c*, (*H. C. Cooper and Others: Thermal Behavior and Optical Properties, J. Am. Chem. Soc.*, **42**, 461, and **47**, 273.)

volume. If the application of heat is not uniform, an apparent bending will take place in the direction of greatest shrinkage.

The second stage is the bending period. This lies just beyond the pyroplastic condition, because the amount of fluid is great enough to cause deformation under its own small weight; yet in most cases the cone in the act of bending contains both solid and fluid matter. The action is that of a viscous liquid. Since the cone has the shape of a

tetrahedron, the tip, having the smallest cross-section and being in a more exposed condition, becomes fluid in the shortest time and starts to bend in the direction of inclination. If the conditions are uniform, each lower section successively joins in the bending motion until the tip has reached the level of the base. Surface tension must assist somewhat in the curving of the cone, for once the bending motion has started there is a tendency for the tip to curve in toward the base of the cone.[1] This action is more noticeable with some cones than with others, the content of raw kaolin apparently increasing the amount of inward curve.

Although the cone is officially "down" when its tip has reached the level of the base, yet some information can be obtained by its condition after this point or during the *flowing stage*. The edges gradually lose their sharpness, the open space under the cone closes, and the mass becomes a shapeless puddle of fluid.

Bending may be retarded or accelerated by endothermic, exothermic, or other reactions, which vary the uniform production of a fluid or its viscosity. Some of the most refractory cones do not describe approximate circles in bending but slump down into a rounded mass after the softening of the tip, similar to the melting of a true compound.

Composition of the Standard Orton Cones.—While the composition of the Orton cones is a secret with the manufacturers, yet a rough idea can be obtained from the older German series[2] and the recent work of the United States Bureau of Standards.[3] 022 is made entirely of a soft glass to which clay is added up to cone 016. Ries[4] gives the molecular composition of Seger's glass as:

$$0.5Na_2O \quad 2.0SiO_2$$
$$0.5PbO \quad 1.0B_2O_3$$

[1] Wilson, Hewitt: "Deformation of Kaolin-feldspar Mixtures, *Trans. Am. Ceram. Soc.*, **15**, 228 (1913).

[2] Ries, H.: "Clays Occurrence, Properties and Uses," 181, John Wiley & Sons, Inc. (1914).

[3] Fairchild, C. O., and M. F. Peters: "Characteristics of Pyrometric Cones," *J. Am. Ceram. Soc.*, **9**, 701 (1926).

[4] Ries, H.: "Clays, Occurrence, Properties, and Uses," p. 181, John Wiley & Sons, Inc. (1914).

A different glass is used between cones 015 to 011. The series again changes at 010, and from there to 01 is a complex mixture of glass, feldspar, iron oxide, whiting, kaolin, and flint or the component oxides are soda, lime, boric, potash, iron, alumina, and silica. Those cones containing iron are red in color, the remainder are white. A feldspar, lime, iron, kaolin, and flint series is maintained in cones 1, 2, and 3; cone 4 is unique but without iron; cones 5 to 28 form a new series consisting of feldspar, lime, clay, and silica with increasing amounts of alumina and silica; cones 29 and 30 contain only clay, flint, and feldspar; cones 31 to 34 contain only clay and flint; cone 35 is pure Florida kaolin and cones 36 to 42 contain only clay and alumina with increasing amounts of alumina. Cones 31 to 42 are therefore a portion of the alumina-silica system.

Deformation Temperatures of Pyrometric Cones.—In the following table are given the temperatures of the Orton series for two rates of heating, 20 and 150° C. per hour. These rates were maintained for some time before and during the bending of the cones, and the temperatures were determined under standardized and reproducible conditions. The cones were heated in clean air, free from carbon and sulphur gases, and at carefully regulated rates of heating. Since the invention of the cone system, continual discrepancies have been noted between cones and their fusion temperatures. In the early days, the cones were not alone at fault because of the inaccurate methods for measuring high temperatures. Again, the cones may show variable deformation temperatures owing to variation in shape and size, composition, structure, raw materials, and methods of manufacture. Different temperatures may be obtained with the best of cones by variations in rate of heating and composition of the furnace gases.

In general, the slower the rate of heating, the lower will be the temperature required for deformation. In the following table the maximum difference is only 58° C., and in but five cases is the difference more than 40°.

TABLE XXVIII.—DEFORMATION TEMPERATURES OF THE ORTON PYROMETRIC CONES[1]

(Decorating-kiln Series (*Hecht*))

Cone number	20° C. per hour rate of heating			150° C. per hour rate of heating		
	End-point, degrees Centigrade	End-point, degrees Fahrenheit	Bending interval, degrees Centigrade	End-point, degrees Centigrade	End-point, degrees Fahrenheit	Bending interval, degrees Centigrade
022	585	1085	45	605	1121	55
021	595	1103	45	615	1139	45
020	625	1157	30	650	1202	25
019	630	1165	30	660	1220	20
018	670	1238	30	720	1328	30
017	720	1328	30	770	1418	30
016	735	1355	35	795	1463	55
015	770	1418	30	805	1481	45
014	795	1463	45	830	1526	40
013	825	1517	45	860	1580	50
012	840	1544	50	875	1607	85
011	875	1607	65	905	1661	65
(Low-temperature Series (*Cramer*))						
010	890	1634	30	895	1643	25
09	930	1706	35	930	1706	40
08	945	1733	55	950	1742	60
07	975	1787	35	990	1814	50
06	1005	1841	25	1015	1859	35
05	1030	1886	30	1040	1904	30
04	1050	1922	40	1060	1940	40
03	1080	1976	40	1115	2039	35
02	1095	2003	35	1125	2057	35
01	1110	2030	50	1145	2093	45
(Medium-temperature Series (*Original Seger*))						
1	1125	2057	30	1160	2120	45
2	1135	2075	30	1165	2129	45
3	1145	2093	30	1170	2138	40
4	1165	2129	40	1190	2174	35
5	1180	2156	40	1205	2201	50
6	1190	2174	40	1230	2246	35
7	1210	2210	40	1250	2282	60
8	1225	2237	45	1260	2300	55
9	1250	2282	65	1285	2345	115
10	1260	2300	40	1305	2381	95
11	1285	2345	70	1325	2417	80
12	1310	2390	80	1335	2435	45
13	1350	2462	70	1350	2462	55
14	1390	2534	100	1400	2552	70
15	1410	2570	85	1435	2615	115
16	1450	2642	70	1465	2669	125
17	1465	2669	50–75(?)	1475	2687	125
18	1485	2705	90	1490	2723	85
19	1515	2759	100	1520	2768	70
20	1520	2768	...	1530	2786	30

[1] FAIRCHILD and PETERS: U. S. Bureau of Standards (1926).

TABLE XXVIII.—DEFORMATION TEMPERATURES OF THE ORTON PYROMETRIC CONES.—(*Continued*)

(High-temperature Series (23 *to* 35 *by Seger*, 36 *to* 42 *by Orton*))

Cone number	20° C. per hour rate of heating			600° C. per hour rate of heating		
	End-point, degrees Centigrade	End-point, degrees Fahrenheit	Bending interval, degrees Centigrade	End-point, degrees Centigrade	End-point, degrees Fahrenheit	Bending interval, degrees Centigrade
23	1580	2876	30			
26	1595	2903	10			
27	1605	2921	15			
28	1615	2939	10			
29	1640	2984	30			
30	1650	3002	25			
31	1680	3056	25			
32	1700	3092	15			
33	1745	3173	30			
34	1760	3200	15	1755	3191	
35	1785	3245	15	1775	3227	
36	1810	3290	25	1810	3290	
37	1820	3308	5	1830	3326	
38	1835	3335	15	1850	3362	
39	....	....	...	1865	3389	
40	....	....	...	1885	3425	
41	....	....	...	1970	3578	
42	....	....	...	2015	3659	

Effect of Furnace Gases.—Sulphur gases have a powerful effect on the viscosity of silicate mixtures, for with all the cones tested except number 011, the end-point was raised from 11 to 35° C. when the cones were softened in an atmosphere containing 0.35 per cent SO_2. The laboratory results indicate that most of the cones are not seriously affected by reducing furnace gases if the sulphur gases are absent. If, however, the cone receives a heavy deposit of graphitic carbon in its surface pores by direct exposure to flame, as in the top of a commercial kiln or by the dissociation of hydrocarbons in the early period of firing, the hard crust of carbon will hold the shell of the cone erect even after the center has softened and has flowed from the base.[1]

[1] HENDERSON H. B.: "Discussion of Cones," *J. Am. Ceram. Soc.*, **9**, 740 (1926).

The investigation by the Bureau of Standards shows that almost every cone gives peculiarities in action which make its deformation different from the others. This is to be expected from the variation in composition and the variation in types of silicates which are all combined into one system. Nevertheless, when the cones are heated in clean air under carefully regulated rates of heating, they are fairly accurate devices for measuring temperature. More work should be done in determining these temperatures for different rates of heating in order that these data can be made applicable to commercial kiln work.

Cones for Measuring the Degree of Vitrification of Clays.—While both the deformation of cones and the vitrification of clay are dependent in a similar manner on the rate of heating, yet they are not necessarily equivalent to each other at all rates of heating. For instance, the following data show differences with a fast and a slow rate of heating when nine clays were heated to the same cone:

TABLE XXIX

Clay number	B1[a]	B2[a]	B5[a]	C1	C2	C3	C4	C5	A2[a]
(Linear Shrinkage in Terms of Original Length)									
Short burn[b]	13.8	16.0	11.5	11.0	7.8	12.0	9.6	17.0	
Long burn[c]	15.4	17.7	12.7	9.1	7.1	10.4	9.2	16.3	15.0
Difference	−1.6	−1.7	−1.2	1.9	0.7	1.6	0.4	0.7	
(Transverse Strength in Pounds per Square Inch)									
Short burn	5,800	7,000	4,750	2,400	1,450	3,550	3,000	8,820	
Long burn	8,430	9,450	5,900	2,088	1,332	2,974	2,700	6,754	8,000
Difference	−2,630	−2,450	−1,150	312	118	576	300	2,066	
Approximate corresponding cone difference[d]	4.0	3.2	2.5	3.7	1.5	3.0	1.5	3.5	4.0

[a] These clays were overfired at cone 6. Consequently the shrinkages and strengths were greater in the long burn, as cone 6 represented a point on the descent of the curve and not on the rise.

[b] Short burn to cone 6 in a small muffle test kiln: heating 7 hours, cooling 6 hours, total 13 hours.

[c] Long burn to cone 6 in full-sized terra cotta muffle kiln: heating 70 hours, cooling 80 hours, total 150 hours.

[d] Average cone difference = 3.0 cones.

The more rapid rate of firing to the bending of cone 6 produced in the above nine clays shrinkages and strengths which were greater than those produced by the slower rate by about three cones, estimated from the curves of

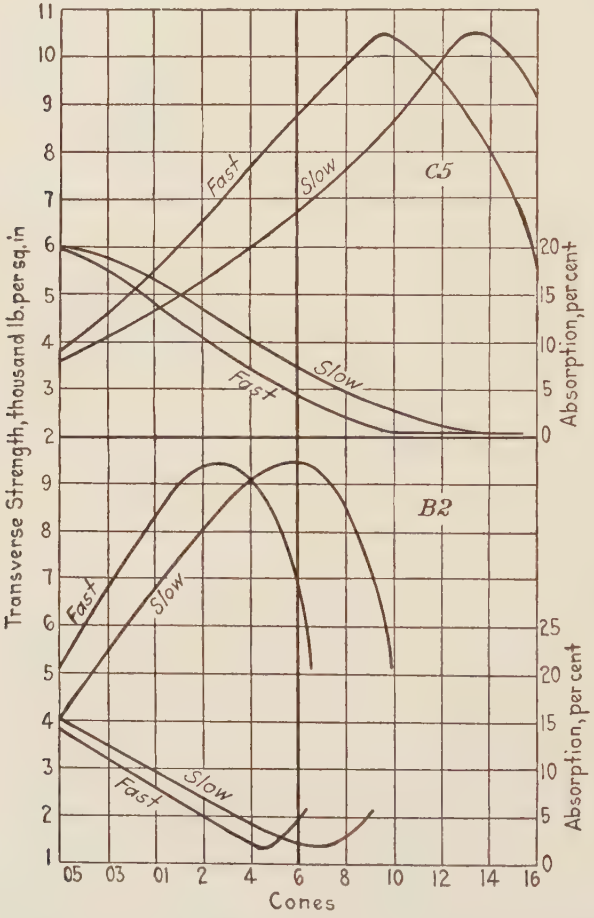


FIG. 91.—Relation between the rate of heating and the degree of vitrification of two clays (measured by changes in strength and absorption) when pyrometric cones are used.

the rapid rate of firing. Apparently from these data the firing to a higher temperature, even though for a shorter time, gave a greater degree of vitrification or fusion. The effect of the "heat work" upon cone 6 was different from

that on the vitrification of the clays. This phenomenon has been noted in the firing of the same terra cotta bodies and glazes in kilns of varying sizes and consequently with different periods of time or rates of heating. If fired to the same cone, the small kilns give evidence of a greater heat effect in the glaze and body development. Hence, the large kilns are fired to higher cones than the smaller ones.[1]

Mellor[2] found similar puzzling data. He noted that the firing shrinkage of the same body was greater when fired to the same cone in a small muffle test kiln in 4 hours than when fired in the large pottery kiln in 3 to 4 days. He states,

> The experimental results show that the vitrification of the body progresses more when heated to the higher temperature for a short time than when heated for a long time at the lower conditions where the work done on Seger's cones is apparently the same.

Heretofore it has been assumed that the two reactions, vitrification of clay and fusion of cone, have the same temperature coefficient, but this is apparently not true for a number of cases.

Fairchild and Peters[3] make similar statements.

> If the ware at a certain schedule of heating is properly matured at the end point of some particular cone, this schedule should be maintained. Experience has shown that if another schedule is followed, the ware may not be properly matured at the same cone. If the same schedule is followed and the kiln gases are the same, the cone will always come down at the same temperature. (Cones thus) . . . measure the temperature at which the ware will mature with a controlled rate of heating and given character of kiln gases. (They do) . . . not measure the combined effect on the ware of time, temperature, and kiln gases . . . It may even be thought by some that in many cases the cone and the ware are so nearly similar that, for practical purposes, they may be regarded as identical, but experience

[1] Facht, Geo. P. Private communication.

[2] Mellor, J. W.: "The Speed of Vitrification of Clays," *Trans. Ceram. Soc.* (*England*), **9**, 80 (1908–1909).

[3] Fairchild, C. O., and M. F. Peters: "Characteristics of Pyrometric Cones," *J. Am. Ceram. Soc.*, **9**, 723, 724 (1926).

proves that this is not the case and that the cone cannot be properly regarded as a true gage of the progress of the maturing of the ware.

Pyrometric Cones as a Measurement of the Refractoriness of a Clay.—The high-temperature series of cones are commonly used in the *cone fusion test* of fire clays and similar refractory materials.[1] The fire clay is ground to pass a 65-mesh sieve, molded into the cone shape, dried, and fired with the standard cones. The nearest cone or cones which approximate the deformation behavior of the fire clay is taken as the refractory value of that material. This test is a good preliminary classification for unknown clays and separates the non-refractory from the possible refractory clays. It should, however, be supplemented by tests under load at high temperatures or heating tests at service temperatures for long periods of time. The result of a deformation test made at cone 31 is no true indication of the refractory ability of that material at the working temperatures between cones 10 and 15. For example, some clays of the stoneware type, which vitrify near cone 8 and which can be deformed by a load of 25 pounds per square inch or less at cone 12 because of the development of pyroplastic material at that heat, may, when in the shape of pyrometric cones, be able to stand under this very small load until cone 31, owing to the high

[1] *Am. Ceram. Soc., Rept. Standards Comm.*, 17 (1921–1922).

Greaves-Walker, A. F.: "The Construction and Operation of a Deville High Temperature Furnace," *Trans. Am. Ceram. Soc.*, **8,** 301 (1906).

Coggeshall, A., and A. V. Bleininger: "A Convenient Carbon Resistance Furnace," *Trans. Am. Ceram. Soc.*, **10,** 55, 1908.

Bleininger, A. V., and G. H. Brown: "Carbon Resistance Furnace," *Trans. Am. Ceram. Soc.*, **12,** 346 (1910).

Wilson, Hewitt: "An Oxygen-acetylene High Temperature Furnace," *J. Am. Ceram. Soc.*, **4,** 836 (1921).

Andrews, Bole and Withrow: "Oxygen-acetylene Furnace," *J. Am. Ceram. Soc.*, **8,** 187 (1925).

Gorton, A. F., and W. H. Groves: "New Type of Oxy-acetylene Fusion Furnace," *J. Am. Ceram. Soc.*, **8,** 768 (1925).

Kanolt, C. W.: "The Arsem Graphite-resistance Furnace," *Trans. Am. Ceram. Soc.*, **15,** 170 (1913).

Helser, P. D.: "Ajax-Northrupp High-frequency Electric Furnace," *J. Am. Ceram. Soc.*, **8,** 822 (1925).

viscosity of the fluid material. The cone-softening test cannot be accepted, therefore, as the final criterion of a refractory clay.

Some fire-clay bodies such as those made of refractory but non-plastic flint fire clay bonded with an inferior plastic fire clay will soften under load at working temperatures with the softening of the plastic bond clay. In other words, the grains of flint clay, although unaffected by the heat, will move over each other in the pyroplastic films surrounding them. In the preparation of cones from such a mixture of refractory and less refractory grains, however, all are ground to pass a 65-mesh sieve, and the resulting cone will give a deformation more nearly like that of the arithmetical proportion of the two clays. Many bond clays are similar to the viscous stoneware type.

The cone fusion test reveals nothing in regard to the physical structure of a finished refractory product or of the past degree of firing. Of course, it alone cannot be expected to tell anything of the resistance of the refractory to thermal shock or to slag action.[1] No one test will reveal the resistance to all the many and varied factors which shorten the life of a refractory. In the past, too much dependence has been placed on the cone fusion test for fire brick. One of the reasons was that satisfactory tests for the other properties had not been developed. In fact, they are being perfected only at the present time. The cone fusion test gives its best service as a means of preliminary classification of an unknown material in order that subsequent testing can be more logically devised. Elimination by the cone fusion test of a material from a refractory class is final, with the possible exception of siliceous bodies, which are given a higher rating if other tests are satisfactory.

Chemical Composition and the Fusion Test of Refractory Clays.—Raoult's law, "that equimolecular portions of different substances produce the same effect on the lowering of the melting point" can possibly be applied only to the melting and softening temperatures of very dilute silicate

[1] This must not be confused with Howe's cone slag test (see R. M. Howe).

solutions. Various German investigators,[1] however, developed general charts for the comparison of molecular compositions to cone fusion determinations. The idea of such a comparison is rather fallacious. It is far easier and cheaper to make a cone fusion determination than the complicated chemical analysis, and, at best, no exact relation ship can be developed between the two determinations. If clays were mixtures of three or possibly four components, an exact relationship could be developed from some of the preceding diagrams.

The best attempt to establish a relationship between the cone fusion point and the composition of refractory clays is purely an empirical one developed by Montgomery and Fulton[2]. The silica-alumina concentration cone diagram gives the maximum fusion points possible with fire clays, which are essentially mixtures of alumina and silica in various mineral combinations. The effect of the fluxes is taken as a reduction from the silica-alumina values in direct relation to the sum of all the fluxes irrespective of their composition. The flux reduction was determined by averaging a large number of direct comparisons when the clays were separated into groups of varying alumina content. It is therefore useful for general comparisons but not for specific comparisons in the same group.

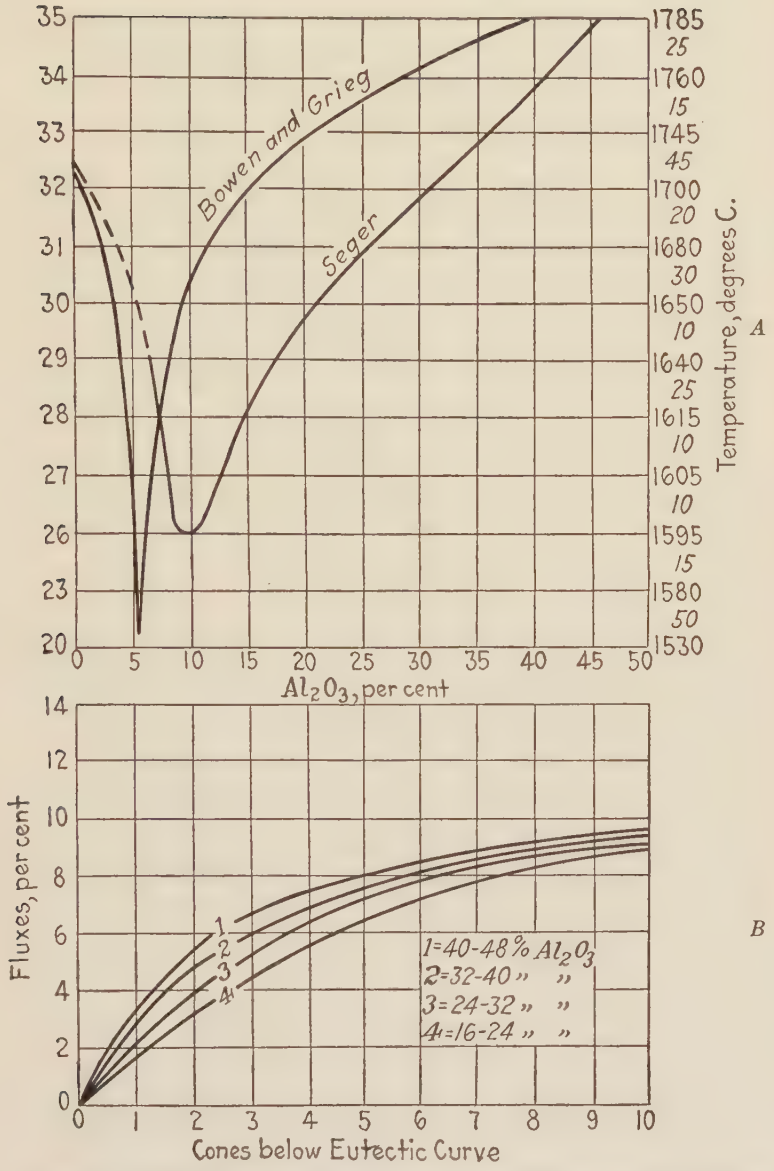
Seger's kaolin-quartz cone curve is shown with Bowen and Grieg's alumina-silica concentration data in Fig. 92*a*. The method of operation is as follows:

1. Determine the per cent alumina plus silica = 100.
2. Note the cone fusion on the curve in Fig. 92*a*.
3. Add the fluxes K_2O, Na_2O, CaO, MgO, Fe_2O_3, and TiO_2.

[1] Richter, Ludwig, Cramer, and Bischof. See Bleininger, A. V.: "Testing of Clay Refractories," *U. S. Bur. Standards, Tech. Paper*, **7**, 33–36 (1912).

Weber, R. F.: "On the Chemical Composition and Refractoriness of Fire Brick," *Trans. Am. Ceram. Soc.*, **6**, 212–226 (1914).

[2] Montgomery, R. J., and C. E. Fulton: "The Relation between the Fusion Point and the Composition of Refractory Clays," *Trans. Am. Ceram. Soc.*, **19**, 303 (1917).



FIGS. 92*A* and 92*B*.—Relation between softening point expressed in both cones and temperatures *versus* composition. The present Orton cone series below cone 31 contains feldspar. (*Seger, Hermann A.: "Collected Writings,"* p. 545.; *Bowen and Grieg: J. Am. Ceram. Soc.*, **7**, 238 (1924) *and Fairchild and Peters: J. Am. Ceram. Soc.*, **9**, 739 (1926) for temperatures of cone-softening points.

4. Note the cone depression corresponding to the total flux content in the diagram of the proper alumina content in Fig. 92*b*.

5. Note the cone fusion after reducing the maximum of Fig. 92*a* by the amount of (4).

Clay is not simply a mechanical mixture of alumina, silica, and fluxing oxides, and the mineral state of the clay composition has been ignored. The above system implies a homogeneous distribution of very finely divided particles. Equal weights of the basic oxides do not exert the same fluxing action on alumina-silica combinations or on each other. The calculation can be made more complicated by the use of factors to correct the errors introduced by the different fluxing actions of the bases, but it would be necessary to bring each clay to the same physical condition. This cannot be obtained by fine grinding alone, but would require repeated fusion and grinding until a homogeneous glass is produced. Such a procedure would mean an entirely new scale of fusion values. When cones are prepared by grinding and remolding the already fused cones, they will be found to deform from two to three cones below the original deformation point.[1]

3. Effect of Pressure on Vitrification and Fusion

"Increase in pressure diminishes the volume, and therefore favors the formation of that system which occupies the smaller volume."[2]

While the boiling point of a liquid is always raised when the pressure is increased, the melting point increases in some cases and decreases in others, but in general only small changes in the melting temperatures accompany large changes in pressure. Clays do not have definite melting points, however, and only their softening behaviors are of interest. Nevertheless, when pressure is applied to a clay during heating, both vitrification and fusion are produced

[1] Wilson, Hewitt: "Deformation of Kaolin-feldspar Mixtures," *Trans. Am. Ceram. Soc.*, **15**, 226 (1913).

[2] Le Chatelier, "Les Equilibres Chimiques," p. 210.

at lower temperatures.[1] This action can be explained by the effect of closer contact between particles for interaction. Deformation is produced as soon as the viscosity developed at any temperature can be affected by the pressure employed. Clays may have from 50 to 200° C. range between the temperature at which softening begins in the vitrification period and the temperature at which the clay begins to flow under its own weight in cone form. By increasing the load, the softening takes place at lower temperatures. The clay during its vitrifying period is in a pyroplastic state with varying yield values for different temperatures, and these need only to be exceeded in order that deformation may be produced. When a load is applied to a silicate mixture, the softening temperature of a low-melting compound or eutectic may be revealed. This was discussed in a previous paragraph with reference to a flint fire clay bonded with a clay of lower refractoriness. Fairchild and Peters,[2] showed the effect of a low-melting glass in cones 08, 09, and 010 by subjecting them to a load which caused all the cones to show bending at 741°, which is the deformation temperature of cone 015.

The load then tends to eliminate the effect of viscosity of the softened portion, and the amount of the fluid phase is not so important. The structure of the clay mass will also greatly influence the results of the high-temperature load test. Other factors being equal, the most compact structure will give the least deformation unless the clay mass is carried to fusion. As shown by M. C. Booze 10)[3] the finely ground, hard-burned brick will give the lowest deformation in the standard load test:

	Per Cent Shrinkage
Finely ground, hard burned	2.76
Finely ground, soft burned	6.92
Coarsely ground, hard burned	4.97
Coarsely ground, soft burned	9.44

[1] Fairchild, C. O., and M. F. Peters: "Characteristics of Pyrometric Cones," *J. Am. Ceram. Soc.*, **9**, 716 (1926).

[2] *Loc. cit.*

[3] Reference 10, page 277.

A soft-burned and porous structure has far less solid matter in contact, and, as soon as a fluid is formed at the surfaces in contact, a sliding action of grain over grain takes place to fill the internal pore space.

The effect of pressure is less on compounds of definite or congruent melting temperatures than with compounds having incongruent melting temperatures or mixtures of compounds, unless the first liquid formed in the latter is

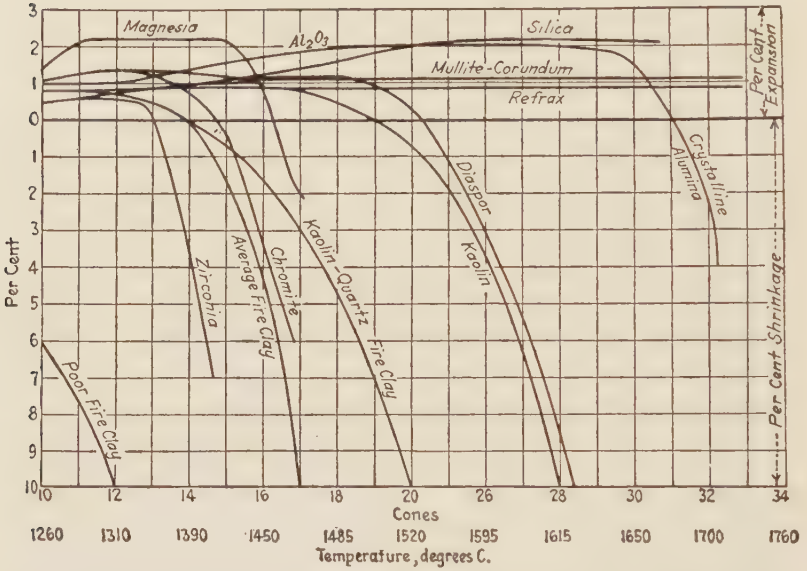


FIG. 93.—High-temperature load tests of various refractory brick, standing on end and subjected to a load of 25 pounds per square inch with increasing temperature. With the exception of the mullite-corundum sample, all are commercial brick. (*Wilson, Hewitt: J. Am. Ceram. Soc.*, **7**, 48 (1924).)

very fluid. In general, bodies made of interlocking crystals are far more resistant to load at high temperatures than are the amorphous bodies (see Fig. 93). This has been noted in the high resistance of silica brick to cone 31, which is close to the melting temperature of the silica-lime composition of the mass. Mullite and carborundum brick will withstand pressure at higher temperatures than silica brick if the interlocking crystallization has been developed, for their melting or dissociation temperatures are higher.

This does not mean, however, that an aggregate of crystalline grains without the interlocking effect will be more resistant than an amorphous material under load. Chrome, magnesia, underfired silica brick, glass-bonded mullite brick will show less resistance to load at high temperatures than many high-grade fire clay or better, the kaolin and diaspor brick.

TABLE XXX

Name	Load-test value[b]	Cone fusion	Per cent maximum expansion	Start of shrinkage cone	Start of fast shrinkage cone	10 per cent shrinkage cone
Refrax	Above 11.8	Dissociation	0.84	Above 33		
Mullite-corundum	11.8	39	1.1	33		
Alumina	11.2	39–40	2.0	29	30	32+ (shear)
Silica	10.62	32–33	2.42	30–31	30–31	31 (shear)
Diaspor	9.38	38	1.12	18	20	28+
Kaolin	7.68	34+	0.85	19–20	23	28+
Kaolin-quartz	4.98	32	0.79	10	16	20+
Magnesia	4.31	.....	2.2	15	15	17 (shear)
Chromite	3.80	42	1.3	10	14–15	16–17(shear)
Average fire clay	3.75	31	0.45	12	14	16–18
Zirconia	2.64	37	0.52	11	13	14–15
Poor fire clay	0.35	28(−)[c]	0.20	Before 10	Before 10	12

[a] See Fig. 93.

[b] The high-temperature load-test value is a comparative figure showing the area under the zero shrinkage line and the shrinkage curve of the refractory in Fig. 93.

[c] The minimum cone fusion of a refractory clay is No. 19

The effect of load on fire-clay bodies is expressed by Mellor and Moore(2) by the following empirical formula:

$$\text{Squatting temperature} = Ce^{-kw}$$

where

C denotes the squatting temperature in cones without load.

w is the load in pounds per square inch.

e is the exponential constant.

k is a numerical constant dependent on the clay and method of manufacture.

From the diagram (Fig. 94) it is seen that the siliceous brick gave less difference between the squatting temperature with and without load.

Mellor states that the more aluminous the fire clay or the more nearly its composition approaches that of china

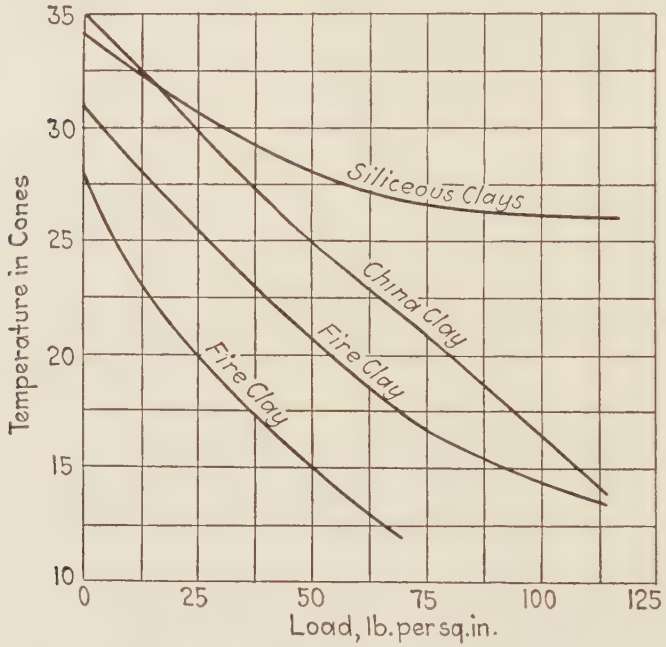


FIG. 94.—(*Mellor and Moore, T. E. C. S.*, **15**, 126 (1916).)

CONES OF FUSION AND VALUES OF k FOR FIG. 94

	k	Cone fusion
Siliceous-clay brick	0.003	34
China-clay brick	0.0082	35
Fire-clay brick	0.0078	31
Fire-clay brick	0.0116	28

clay, the greater the difference between the squatting temperature with and without a load. This may be true for materials like ordinary clay fire brick, but apparently does not apply to the high-aluminous crystalline electric-furnace products such as alundum or mullite(3).

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3. Wilson, Hewitt, C. E. Sims, and F. W. Schroeder: "Sillimanite as a Refractory," *J. Am. Ceram. Soc.*, **7,** 842–855, 907–919 (1924).
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8. "Refractory Materials under Load at High Temperatures," *Am. Soc. Testing Materials, Repts. Comm. C-8* (1920).
9. Wilson, Hewitt: "High Temperature Load and Fusion Tests of Fire Brick from the Pacific Northwest," *J. Am. Ceram. Soc.*, **7,** 34 (1924).
10. Booze, M. C.: "The Load Test for Fire Clay Refractories," *Am. Refractories Inst., Tech. Paper* **2** (1926).

4. Deformation Eutectics

With most silicate mixtures it is possible to determine compositions which have the lowest deformation temperatures of a given series. Such deformation-concentration systems are similar to the previously described temperature-concentration systems with the deformation or fusion of pyrometric cones replacing the melting temperatures. The Seger-Orton cone series itself from cones 31 to 42 follows the alumina-silica concentration diagram (see Fig. 53). The fluxing action of the fluid eutectic is seen very clearly in the deformation of successive cones. While the cone-deformation temperatures, expressed in degrees Centigrade, will vary with the rate of heating and atmospheric treatment, the order of deformation of the cones will remain the same (slight exceptions) and the cone containing the greatest amount of eutectic composition will be able to bend at the lowest temperature.

EXAMPLES OF DEFORMATION EUTECTICS

Reference	Author	Composition, per cent by weight	Fusion temperature, degrees Centigrade, or cone
1	Kirkpatrick	Orthoclase 98.3, CaO 1.7 (Fig. 82)	1261
1	Kirkpatrick	Orthoclase 98.6, MgO 1.4 (Fig. 83)	1271
1	Kirkpatrick	Albite 84.3, CaO 15.7 (Fig. 84)	1157
1	Kirkpatrick	Albite 95.2–90.8, MgO 4.8–9.2 (Fig. 85)	1185
2	Rieke	$Al_2O_3 2SiO_2$ 67.0, CaO 33.0 (Fig. 86)	cone 7
2	Rieke	$Al_2O_3 1SiO_2$ 74.4, CaO 25.6 (Fig. 87)	cone 10
3	Rieke	MgO 30, kaolin 30, quartz 40, or MgO 31, Al_2O_3 13, SiO_2 56	cone 10
4	Seger	Potash feldspar 42.1, whiting 17.7, hydrous kaolin 13.0, flint 27.2	cone 4
5	Watts	Albite 69, microcline 29.0 (Fig. 79)	cone 6
5	Watts	Albite 100, quartz 0.0	cone 6–7
5	Watts	Microcline 90.0, quartz 10	cone 9 plus
6	Wilson	Potash feldspar 90.0, kaolin 10	cone 8 plus
7	Hanna	Canadian feldspar 92.0, Florida kaolin 8.0	cone 6–7
7	Hanna	Canadian feldspar 92.0, ball clay 8.0	cone 6 minus
7	Hanna	Canadian feldspar 96.0, quartz 4.0	cone 6–7
7	Hanna	CaO 23.25, Al_2O_3 14.75, SiO_2 62.0	cone 6 minus
7	Hanna	Feldspar 71.5, $CaCO_3$ 8.6, clay 7.7, flint 12.2	cone 3 minus
8	Watts	MgO 20.0, Al_2O_3 20.0, SiO_2 60.0	cone 12
9	Watts	BaO 35–40, Al_2O_3 10.0, SiO_2 55 to 50	cone 6
10	Watts	ZnO 50.0, Al_2O_3 20.0, SiO_2 30.0	cone 12–13
10	Watts	Canadian spar 59.62, whiting 8.03, zinc oxide 6.50, Florida kaolin 13.81, flint 12.04	cone 03
11	Mellor	PbO 88.0, SiO_2 12.0 (Fig. 90)	532
12	Rice	K_2O 55, SiO_2 45	780
12	Rice	K_2O 17.5, SiO_2 82.5	880
12	Rice	K_2O 17.4, SiO_2 77.4, Al_2O_3 5.2	870[a]
12	Rice	Na_2O 51.5, SiO_2 48.5	830
12	Rice	Na_2O 18.4, SiO_2 81.6	860
12	Rice	Na_2O 17.5, SiO_2 77.1, Al_2O_3 5.4	800
13	Guertler	CaO 35, B_2O_3 65	995
13	Guertler	CaO 47.5, B_2O_3 52.5	1070
13	Guertler	BaO 76.5, B_2O_3 23.5	750
14	Klooster	$K_2O.B_2O_3$ 50, $Na_2O.B_2O_3$ 50	800
15	Wallace	$Na_2O.SiO_2$ 60, $BaO.SiO_2$ 40	
16	Eskola	$CaO.SiO_2$ 27.5, $BaO.SiO_2$ 72.5	
17	Lu	PbO 60.8, Al_2O_3 7.1, SiO_2 31.45	650
17	Lu	ZnO 50.8, Al_2O_3 14.45, SiO_2 35.75	1360
17	Lu	PbO 77.6, B_2O_3 6.1, SiO_2 16.3	415
17	Lu	Na_2O 24.2, B_2O_3 35.2, SiO_2 40.6	570
17	Lu	K_2O 23.7, B_2O_3 37.2, SiO_2 39.1	655

[a] Higher than binary eutectic.

The action of the silica-alumina eutectic was clearly shown by Sosman,[1] who held cones 28, 29,[2] 30, 31, 33, and 34 at 1616° C. for 5 hours, after 1 hour's previous heating and completely deformed all but cones 33 and 34, which had, however, started to bend. The deformation temperature of cone 28 for fast heating is 1616° C. It is to be noted, however, that the cones deformed in numerical order, and the above result does not detract from their usefulness in the ceramic industry.

The pyrochemical changes during the heating of these cones is as follows: On heating under equilibrium conditions, quartz inverts to tridymite at 870° C. and tridymite in turn to cristobalite at 1470°. In fast heating the quartz may go into solution as such or may skip the tridymite stage and invert directly to cristobalite. Kaolin dehydrates at 500° and dissociates at 900° (plus) into mullite and silica. Orton cones above number 23, however, are prepared for the market in the calcined condition. Mullite, $3Al_2O_32SiO_2$, and excess cristobalite then melt to form the eutectic at 1545° C., which gradually fuses into or softens the whole cone mass. Near 1816°, the remaining mullite melts incongruently, leaving alumina or corundum and liquid to replace it.

The above changes are the theoretical activities which take place slowly and undoubtedly are hurried over in an incomplete fashion in most laboratory testing.

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[1] Sosman, R. B.: "Physical Chemistry of Seger Cones," *Trans. Am. Ceram. Soc.*, **15**, 482 (1913).

[2] In the Seger series, cones 28, 29, and 30 did not contain feldspar but only clay and silica.

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5. Comparison between the Theoretical Melting Temperatures and Softening Temperatures

It is interesting to note the close comparison between the melting-point eutectic compositions obtained by the quenching-crystallization method and the fusion or deformation eutectic compositions obtained by the cone fusion method. The two cases of special note are those of Seger's kaolin-quartz system[1] and A. S. Watts' magnesia-silica-alumina system[2] in comparison with the melting-point data obtained by the Geophysical Laboratory.[3] Both Seger's and Watts' work was done before that of the Geophysical Laboratory. Rieke in 1906 also made an excellent study of the kaolin-lime series by the cone method.

Feild and Royster[4] found the temperature-viscosity values for a number of compositions in Rankin and Wright's lime-alumina-silica temperature-concentration system.

[1] Seger, Hermann A.: "Collected Writings," **1,** 545.

[2] Watts, A. S.: "Magnesia, Alumina, and Silica Deformation Study," *Trans. Am. Ceram. Soc.*, **19,** 453 (1917).

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[4] Feild, A. L., and P. H. Royster: "Temperature-viscosity Relations in the Ternary System, CaO-Al_2O_3-SiO_2," *U. S. Bur. Mines Tech. Paper* **189** (1918).

These data indicate that at the same temperature lower viscosities will be found with those compositions higher in lime than that of Rankin and Wright's ternary eutectic. Figure 95 was made from data given by Feild and Royster for viscosities at 1400° C. The figures along the four boundary curves represent viscosities and show maximums (marked *H*) at the quintuple points and minimums (marked

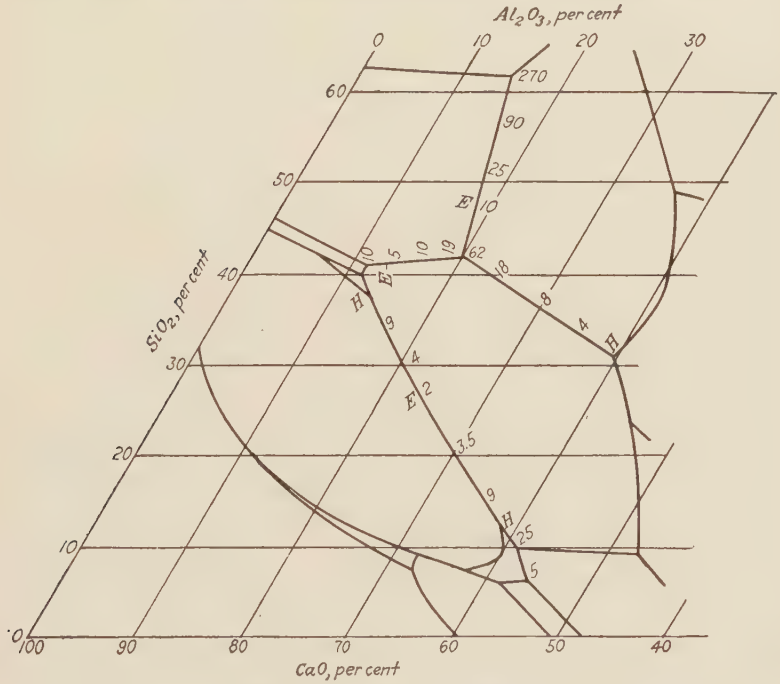


FIG. 95.—(*Field and Royster.*)

E) at the binary eutectics. Data were found which indicated the existence of compounds in the liquid state. The viscosity of fluid silicates usually varies inversely as the temperature and becomes infinite asymptotically to the melting temperature. The work of Feild and Royster indicates that the viscosity of the ternary eutectic mixtures becomes so great that crystallization can occur only with the greatest difficulty. Points (6) and (14) are two reported exceptions, which have low viscosities similar to

those of the binary eutectics. With most ceramic materials, viscosity data are more important than crystallization data in the temperature-concentration systems.

H. ELECTRICAL CONDUCTIVITY AND THE HEATING OF CLAYS AND SILICATES

Barus and Iddings[1] have shown that silicate melts and volcanic magmas possess electrical conductivity, and Doelter proved that melted basalt can be electrolyzed by obtaining an accumulation of iron at the cathode. Fused silicates thus behave as electrolytes and represent dissociated solutions.

Kinnison[2] measured the conductivity of Bedford shale and a porcelain body and found that while these bodies were nonconductors at ordinary temperatures, the conductivity increased very rapidly up to about 1000° C. and was then practically constant with less than 4000 ohms resistance (½-inch thickness) with increase of temperature. The resistance while the sample was all solid and had a high temperature coefficient was quite different from that after fusion had started and when the current could be carried by the fused portion. In more recent work,[3] a carbon train carries the current between the electrodes until the silicate mass is fused. Bleininger[1] suggested that the softening point of the principal composite eutectic of the clay could be determined in such a manner.

[1] *Am. J. Sci.*, **44**, 242 (1892).

[2] Kinnison, C. S.: "The Electrical Conductivity of a Porcelain Mixture and a Shale on Heating," *Trans. Am. Ceram. Soc.*, **17**, 421 (1915).

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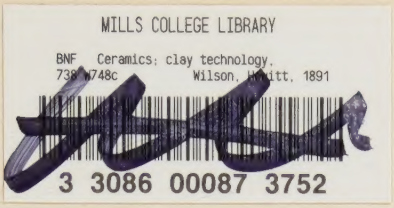
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